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Determination of potentially toxic elements (PTEs) and an assessment of environmental health risk from environmental matrices

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The thesis submitted in partial fulfilment of the requirements of Northumbria University, Newcastle upon Tyne for the degree of Doctor of Philosophy

June 2010

Declaration

This thesis records the results of experiments conducted by myself in the School of Applied Sciences, Northumbria University under the supervision of Prof. John R. Dean and Dr Jane Entwistle between September 2006 and June 2010. It is of my own composition and has not previously been submitted in part, or in whole, for a higher degree.

Abstract

A former industrial site now used for recreational activities was investigated for total PTE content, uptake of the PTEs by foraged fruits and mobility of the PTEs using single extraction such as HOAc and EDTA. In order to evaluate the health risks arising from ingestion of the PTE contaminated soil, the oral bioaccessibility using *in vitro* physiologically based extraction test (PBET) and tolerable daily intake (TDI) or mean daily intake (MDI) was used. The PBET simulates the transition of the PTE pollutants in the soil into human gastrointestinal system while the TDI or MDI is the mass of soil that a child would require to take without posing any health risk. In addition to the former industrial site, an investigation of the urban road dust from Newcastle city centre and its environs was undertaken with the view to looking into the PTE content, oral bioaccessibility and the platinum group elements (PGEs).

Optimized microwave procedure was applied to 19 samples obtained from a former industrial site (St Anthony's lead works) in Newcastle upon Tyne. Of the range of PTEs potentially present at the site as a consequence of former industrial activity (As, Cd, Cr, Cu, Ni, Pb and Zn), the majority of top soil samples indicated elevated concentrations of one or more of these PTEs. In particular, data obtained using either inductively coupled plasma mass spectrometry (ICP-MS) or flame atomic absorption spectroscopy (FAAS) indicates the high and wide concentration of Pb on the site (174 to 33,306 mg/kg). Comparing the resulting PTEs data with UK Soil Guidelines Values (SGVs) suggests at least parts of the site represent areas of potential human health risk. It was found that Pb soil values exceeded the SGV on 17 out of the 19 sampling sites; similarly for As 7 out of 19 sampling sites exceeded the SGV. While for Cd and Ni the soil levels were below the stated SGVs.

Samples of foraged fruits collected from the same site were also analysed for the same PTEs. The foraged fruit was gathered over two seasons along with samples of soil from the same sampling areas, acid digested using a microwave oven, and then analysed by ICP-MS. The foraged fruits samples included blackberries, rosehips and sloes which were readily available on the site. The concentration levels of the selected elements in foraged samples varied between not detectable limits and 24.6 mg/kg (Zn). Finally, the soil-to plant transfer factor was assessed for the 7 elements. In all cases, the transfer values obtained were below 1.00,

except Cd in 2007 which is 1.00, indicating that the majority of the PTE remains in the soil and that the uptake of PTE from soil to plant at this site is not significant.

The determination of total or pseudo total PTE content of soil is often insufficient to assess the risk to humans. A range of extraction protocols were applied to the 19 samples urban topsoils, and report on the correlations between pseudo total PTE content and results obtained following a physiologically-based extraction procedure (oral bioaccessibility), EDTA and HOAc extraction protocols (reagent-specific available fraction), for a broad range of PTEs (As, Cd, Cu, Cr, Ni, Pb, Zn). Results of the single-reagent extraction procedures did not, in general, provide a good indication of oral bioaccessibility but shows positive correlation with the pseudo total PTE content. The bioaccessibility data shows that considerable variation exists both spatially across the site, and between the different PTEs, but correlates well with the pseudo-total concentrations for all elements (r^2 exceeding 0.8). One of the main objectives of this work is to show the role of bioaccessibility in generic risk assessment. Comparison of the pseudo-total PTE concentrations with SGV or generic assessment criteria (GAC) indicated that all of the PTEs investigated need further action, such as receptor exposure modelling. If we refine our generic risk assessment using the PTE bioaccessibility data then a very different picture of the site emerges; one where 5 out of the 7 PTEs investigated indicate the need for a more detailed site-specific risk assessment showing that bioaccessible fraction instead of pseudo total PTE content allows a more considerable approach to human health risk assessment to be made.

Potential health risk from the site was also calculated to estimate the mass of soil a child would require to ingest to reach the estimated TDI or MDI. From the results for a child with geophagy (50 g/day) behaviour the levels of all PTEs are exceeded except Cr (III). In contrast for a child with pica behaviour (1 g/day) only two PTE exceeds the TDI value i.e. Cd and Pb; in addition, for As, the ID_{oral} value and the MDI values are exceeded. Based on the unintentional consumption of 0.1 g of soil, only Pb and As exceed the guideline value (TDI and ID_{oral} respectively) for this type of samples.

The pseudo-total and bioaccessible concentration of 6 PTEs in urban street dust from nine sampling sites across Newcastle upon Tyne city centre and its environs was investigated. Typical pseudo-total concentrations across the sampling sites ranged from 4.4 to 8.6 mg/kg for As, 0.2 to 3.6 mg/kg for Cd, 25 to 217 mg/kg for Cu, 14 to 46 mg/kg for Ni, 70 to 4261

mg/kg for Pb, and, 111 to 652 mg/kg for Zn. This data compared favourably with other urban street dust samples collected and analysed in a variety of cities globally, the exception was the high level of Pb determined in a specific sample in this study. The concentration of PTEs in the samples has been compared to estimated tolerable daily and mean daily intakes values against recommended ingestion values for geophagy behaviour, soil-pica behaviour and unintentional consumption. Based on the unintentional consumption of dust samples (0.1 g/day) no PTE exceeded the guidelines values. The oral bioaccessibility of PTEs in street dust was assessed using PBET. Based on a worst case scenario the PBET approach estimated that Cd and Zn had the highest % bioaccessible fractions (> 45%) while the other PTEs i.e. As, Cu, Ni and Pb had lower % bioaccessible fractions (< 30%). It was postulated that Cd and Zn were more likely to be derived from anthropogenic sources whereas the other PTEs were more indicative of both anthropogenic and natural sources. The bioaccessible concentration was compared to the guideline values based on the unintentional consumption (0.1 g/day). In all cases the bioaccessible concentration values were well below the guideline values.

The concentrations of PGE (Rh, Pd and Pt) were measured in the 9 sampled points of urban road dust from the Newcastle city centre. The result reveals that the concentration of Rh ranges from 1.2 to 54.8 ng/g, Pd from 2.7 to 203.7 ng/g and Pt from 8.1 to 118.5 ng/g. The mean value of Pd (79.8 ng/g) is significantly higher than those of Rh (17.6 ng/g) and Pt (38.2 ng/g) showing a shift from Pt to Pd in its use in the construction of catalytic converters. The grain size analysis was carried out using three dust samples. The three samples were fractionated into six size fractions with their sedimentological equivalent in parenthesis: 1000-2000 μm (very coarse sand), 500-1000 μm (coarse sand), 250-500 μm (medium sand), 125-250 μm (fine sand), 63-125 μm (very fine sand) and <63 μm (silt and clay). The typical relationship in grain size analysis is that concentration of the metal increases with decreasing grain size. On this basis, most of the dominant fraction analysed for PGEs in soils by many researchers is the <63 μm size fractions. However, this assumption is called into question in the present study as the result obtained shows that reasonable concentration of PGEs can be obtained in other size fractions especially the 63-125 μm hence analysis of only < 63 μm fraction will underestimate the PGE concentration in the environmental sample.

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Chapter One: Environmental significance of PTEs in urban soils and dust

1.1 Introduction

The study of urban soils and dusts is becoming increasingly important because the PTE content of soil/dust in urban environments is typically elevated as a result of anthropogenic inputs such as traffic emissions (vehicle exhaust particles, tire wear particles, weathered street surface particles, brake lining wear particles), industrial emissions and historic legacy (power plants, coal combustion, metallurgical industry, auto repair shop, chemical plant, etc), domestic emissions, weathering of building and pavement surface and atmospheric deposits (1). These anthropogenic inputs stem from increases in population and rapid economic development globally. As a result of the increase in percentage of the population living the cities, the environmental quality of urban soils is becoming very important with regards to human health (2). Urban soils are characterised by unpredictable soil structures, higher pH, low organic matter as well as high concentration of trace elements compared to natural soil (3, 4). These characteristics are as a result of urban development coupled with historical/industrial activities carried out in urban areas and can lead to consequences such as hazards in construction projects and adverse effect on buildings and building materials. Also to be affected are the flora and fauna potentially resulting in the bioaccumulation of contaminants in plants, fruits and vegetables entering the human food chain (5). Urban soils/dust are valuable indicators of the urban environment. They can be freely inhaled (the fine portion), adhere readily to hands, body and clothes and hence are liable to be ingested and can easily be washed away by rain to the aquatic environment thereby potentially polluting the water. Top soils and roadside dusts in urban area are indicators of potentially toxic element (PTE) contamination from atmospheric deposition (6). The PTE content in urban soil/dust are commonly studied soil pollutants because they are ubiquitous, toxic and persistent. They cannot be degraded to non toxic forms by either biological or chemical means thus may either accumulate locally or be transported over long distances. Once they contaminate the ecosystem, they remain a potential threat for many years. They may be of geological origin entering into the soil system by weathering or anthropogenic activities such as mining, industrial processing, agricultural run-off and sewage disposal. The rapid development and increase in mining and industrial activities have gradually redistributed many of the PTEs from the earth's crust to the environment hence has substantially raised the chances of human exposure to these elements through ingestion, inhalation or skin contact. Potentially toxic elements can be retained by soils and /or mobilised to soil solution by

biological and chemical mechanisms with a potential impact on human health. When the PTE contamination is very high (thousands of mg/kg) and the metal sorption capacity of the soil is exceeded, PTEs in soils can runoff into rivers or lakes or leach into the ground water, causing accumulation in animals, plants and people (7). The most common PTE listed by the United States Environmental Protection Agency (USEPA) are arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu) nickel (Ni), lead (Pb) and zinc (Zn). Some of these PTEs are essential for the metabolism of living organisms. Potentially toxic elements such as Cr, Cu, Ni and Zn are required by organisms at low level and become toxic at some higher levels of exposure. Non-essential elements including As, Cd and Pb are toxic and not required by organisms at any level. Table 1.1 shows some of the industrial uses and sources of these elements. Above a certain concentration, all PTEs have adverse effects (Table 1.2) on human health (8-11). The hazard imposed by PTE contaminants within the soil is dependent on their ability to migrate into the water system and their availability for biological uptake. The degree to which a contaminant may dissociate from soil solids and become available to a target organism (i.e. bioaccessibility) is therefore a determining risk factor (12).

Another important group of elements with respect to their concentration in urban soils/dust are the platinum group elements (PGEs). These groups of elements can be found in urban soils/dust as a consequence of the deposition from cars fitted with catalytic converters.

1.2 Solid phase partitioning

The manner in which an element is bound to the soil components or other environmental solids, influences the mobility and, ultimately, the bioavailability and toxicity of the element to organisms (13). PTE cations can occur in many geochemical forms: free or complexed ions in soil solution, ions held to charged surfaces (exchangeable) and metal hydroxides and carbonates (14). PTEs may also be associated with Fe and Mn oxides and Al hydroxides, can be bound within organic matter and also can be incorporated into sulphides and bound within lattice structure of soil. Some potentially toxic elements are weakly bound to the solid phase hence have greater potential to be easily extracted i.e available. As a result, their toxic effects to the environment start earlier than those released in the later stage.

The release of these PTEs from the solid phase depends on the strength of the reagents used in the process. Normally the reagents are targeted to remove the analyte of interest in the

specific phase either by exchange process or dissolution of the target phase. The solid phase partitioning depends greatly in soil pH and organic matter content (13).

1.3 PTEs in urban soils and dusts

A brief review regarding the occurrence in soil, uses, deficiency and toxicity of each of the most common PTEs is presented as follows:

1.3.1 Arsenic (As)

Arsenic is a semi metallic element that occurs in a wide variety of minerals, mainly as As_2O_3 , and can be recovered from processing of ores containing mostly Cu, Pb, Zn, Ag and Au. It is also present in ashes from coal combustion. According to its oxidation state, As occurs in nature as arsenate (As^{5+}), arsenite (As^{3+}), arsenic metal (As^0), and arsine (As^{3-}).

Table 1.1: Industrial uses of some PTEs (15).

PTE	Industrial Uses
As	Pesticides/herbicides, glass and ceramic works, traditional medicines.
Cd	Electroplating, storage batteries, stabilisers, solar cells, pigments, alloys for telegraph and telephone wires, photoelectrical and electron optical devices, nuclear reactors
Cr	Alloying additives to stainless steel, chrome plating, dyes, pigments, tanning of leather, textiles, cassette tapes, magnetic storage media for computers, matches, pyrotechnics, photography, seed disinfection.
Cu	Electrical goods, kitchenware, alloys, algacides/fungicides, pigments, supplement in deficient pastures, intra-uterine contraceptive devices.
Ni	Alloys for corrosion resistant equipment. Cooking utensils, coinage, heating elements, gas turbines, jet engines, electroplating, paints, pigments, batteries.
Pb	Storage batteries, antiknock agent in petroleum/gasoline, paints, ammunition, glassware, ceramics, protection from radiation, bearing alloys, rubber industry, printing press.
Zn	Galvanising of iron and steel for corrosion protection, alloys, vulcanization of rubber, photocopying paper, paints, TV tubes, rayon glass, enamel and plastic industries, fertilisers, medicine and cosmetics.

Among these, most investigations on As geochemistry have focused on As^{5+} and As^{3+} because natural occurrence of As^0 is rare and As^{3-} exists only under highly reducing conditions.(16) A wide range of As concentrations has been reported in soils around the world with an average of $5\text{--}10 \text{ mg kg}^{-1}$ in uncontaminated soils (16). Arsenic may accumulate in soils due to agricultural practices such as the applications of As-containing

Table 1.2: Toxicity of major potentially toxic elements (PTEs) in polluted soils (8-11).

PTE	Toxicity	Human toxicity	Zoo toxicity	Phyto toxicity
As	Various skin lesions appear (after several years of low arsenic exposure): hyperpigmentation, ie dark spots, hypopigmentation, ie white spots and keratoses of the hands and feet. After a dozen or more years skin cancers are expected . Longer exposures may lead to cancers of the lungs, kidneys, liver and bladder.	H	M	L
Cd	Nephropathy, pulmonary lesions and lung cancer	M	M	
Cr	Allergic contact dermatitis, possibly carcinogenic in some cases of workers being exposed, mostly because of Cr^{+6}	H	M	L
Cu	Cu is absorbed primarily from food. The toxicity for human is not very high.		H	M
Ni	The toxicity for humans is not very high, but it can cause respiratory diseases.			M
Pb	Lead can be very toxic for human health. For children: reduction in intellectual quotient, hyperactivity, hearing loss. For adults: increased blood pressure; liver, kidney and fertility damage.	M	M	
Zn	Zinc deficiency may also be a problem for human health. At high doses Zn may interfere with calcium metabolism and impair immune responses.			H

H = high; M = moderate: L = low.

pesticides and herbicides, pig manure, and phosphorus fertilizers, thereby raising concerns about the risk of As to the environment and human health (16-21). The accumulated As in soils can distribute among different soil components, such as organic matter, Fe and Mn oxides, carbonates and sulphides, and such distribution could affect its mobility, bioavailability and toxicity (16, 22-24).

Though both aqueous As^{5+} and As^{3+} are highly toxic to organisms, As^{3+} has 200 times higher toxicity than As^{5+} at the same concentration (25, 26). In addition to its toxicity, As^{3+} has enhanced mobility in natural water system and this mobility increases as pH increases (27, 28). Under reducing conditions As^{3+} dominates, existing as arsenite (AsO_3^{3-}) and its protonated forms: H_3AsO_3 , H_2AsO_3^- , HAsO_3^{2-} . Arsenite can adsorb or co-precipitate with metal sulphides and has a high affinity for other sulphur compounds.

In aerobic environments, As^{5+} is dominant, usually in the form of arsenate (AsO_4^{3-}) in various protonation states: H_3AsO_4 , H_2AsO_4^- , HAsO_4^{2-} , AsO_4^{3-} . Arsenate, and other anionic forms of As behave as chelates and can precipitate when metal cations are present (29). As^{5+} is readily immobilized on soil and sediment particles by adsorption on and co-precipitation with oxides of Mn, Al and Fe under acidic and moderately reducing condition (30, 26). Arsenate (As^{5+}) can also be mobilized under reducing conditions that encourage the formation of As^{3+} , under alkaline and saline conditions, in the presence of other ions that compete for sorption sites, and in the presence of organic compounds that form complexes with As (27, 28). Arsenates can be leached easily if the amount of reactive metal in the soil is low.

Studies on the geochemical behaviour of As during the past decade have revealed that microorganisms play a significant role in electrochemical speciation and cycling of As in nature by mediating the transformation of As and As-adsorbents (31, 26). Elemental arsenic and arsine, AsH_3 , may be present under extreme reducing conditions. Sorption and coprecipitation with hydrous iron oxides are the most important removal mechanisms under most environmental conditions (28, 32, 33).

Tolerable daily intake (TDI) and mean daily intake (MDI) indicates the quantity of soil a child is required to take in a day without running the risk of being harmed. These values have been used to assess the potential health risk to a child. In the case of As, a non-threshold carcinogen, TDI is inappropriate hence an oral index dose (ID_{oral}) has been proposed of 0.3

µg/kg bw/day (34). Therefore the ID_{oral} value based on an assumed body weight of 10 kg child is 3 µg/day and MDI 5 µg/day based on 20 kg child (34).

1.3.2 Cadmium (Cd)

Cadmium is soluble in acids but not in alkalis. It is similar in many respects to Zn but it forms more complex compounds. Cadmium occurs naturally in the form of cadmium sulphide or carbonate (CdS or CdCO₃). It is recovered as a by-product from the mining of sulphide ores of Pb, Zn and Cu. Sources of Cd contamination include plating operations and the disposal of Cd-containing wastes (27, 28). The most common form of Cd include Cd²⁺, cadmium-cyanide complexes, or Cd(OH)₂ solid sludge (27, 28). Adsorption mechanism is the primary source of Cd removal from the soil (35,36). The chemistry of cadmium in the soil environment is to a great extent controlled by pH. Under acidic conditions Cd solubility increases and very little adsorption of Cd by soil colloids, hydrous oxide and organic matter takes place. At pH values greater than 6, Cd is adsorbed by the soil solid phase or is precipitated, and the solution concentration of Cd is greatly reduced. Cd forms soluble complexes with inorganic and organic ligands, in particular Cl⁻. The formation of these complexes will increase the mobility of Cd in soil. Hydroxide and carbonate of Cd solids dominate at high pH. Cadmium will also precipitate in the presence of phosphate, arsenate, chromate and other anions. Cadmium is relatively mobile in surface water and ground-water systems and exists primarily as hydrated ions or as complexes with humic acids and other organic ligands (28). Sorption is also influenced by the cation exchange capacity (CEC) of clays, carbonate minerals, and organic matter present in soils and sediments. Under reducing conditions, precipitation as CdS controls the mobility of cadmium (27, 28). Cadmium salts with low solubility includes cadmium phosphate (Cd₃(PO₄)₂), sulphide (CdS), hydroxide (Cd(OH)₂ and carbonate (CdCO₃). The solubilities of these Cd salts will increase with decreasing pH.

The TDI for Cd based on a 10 kg child is 5 µg/day (37) and for MDI is 28.7 µg/day based on a 20 kg child (38).

1.3.3 Chromium (Cr)

Chromium does not occur naturally in elemental form but only in compounds. It is mined as a primary ore product in the form of the mineral chromite, FeCr₂O₄. Major sources of Cr contamination include releases from electroplating processes and the disposal of Cr

containing wastes (27). Chromium is unstable in O_2 , it immediately produces a thin oxide layer that is impermeable to oxygen and protects the metal below. Chromium exists in the environment in two stable oxidation states, Cr^{6+} and Cr^{3+} , which have different toxicity and transport characteristics.

Chromium in oxidation state of +6 is the form of Cr commonly found at contaminated sites (28). Hexavalent chromium, Cr^{6+} , typically exists as the oxyanion chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$) and precipitate readily in the presence of metal cations such as Ba^{2+} , Pb^{2+} , and Ag^+ . Chromate and dichromate also adsorb on soil surfaces especially Fe and Al oxides. The hexavalent Cr has a high solubility in soils (at a high soil pH) and waters and tends to be mobile in the environment. Additionally, it is acutely toxic, subject to biological uptake, and also carcinogenic (39). Chronic exposure to hexavalent Cr is reported to induce renal failure, anaemia, haemolysis and liver failure.

In contrast, Cr^{3+} , is the dominant form of Cr at low pH (<4). Chromium in oxidation state of +3 has a limited hydroxide solubility and forms strong complexes with ions such as NH_4^+ , Cl^- , F^- , CN^- , SO_4^{2-} making it relatively immobile and less available for biological uptake. Cr^{+3} is an essential trace element to humans and shortages may cause heart conditions, disruptions of metabolisms and diabetes. Uptake of excess Cr^{3+} can cause health effects e.g. skin rashes. Therefore, reduction of Cr^{6+} to Cr^{3+} is considered an important remediation strategy for reducing the deleterious effects of this pollutant. Cr^{6+} can be reduced to Cr^{3+} by soil organic matter, S^{2-} and Fe^{2+} ions under anaerobic conditions.

The TDI of Cr^{3+} based on a 10 kg child is 50 $\mu g/day$ for soluble compounds and 50,000 $\mu g/day$ for metallic and insoluble compounds (37). The MDI for Cr^{3+} is 60.2 $\mu g/day$ and 6.7 $\mu g/day$ for Cr^{6+} (38).

1.3.4 Copper (Cu)

Copper is a very common substance that occurs naturally in the environment and is distributed through natural phenomena (wind-blown dust, decaying vegetation, forest fires and sea spray) and human activities (mining, metal production, wood production and phosphate fertilizer production). Copper is mined as a primary ore product from CuS and oxide ores. Mining activities are the major source of Cu contamination. Other sources of Cu include algacides and Cu pipes. Copper has low chemical reactivity. In moist air it slowly

forms a greenish surface; this coating protects the metal from further attack. Copper can be found in many kinds of food, in drinking water and in air; as a result we absorb quantities of Cu each day by eating, drinking and breathing. The absorption of Cu is necessary, because it is a trace element that is essential for human health. Solution and soil chemistry strongly influence the speciation of Cu. In aerobic, sufficiently alkaline systems, CuCO_3 is the dominant soluble copper species. The cupric ion, Cu^{2+} , and hydroxide complexes, CuOH^+ and $\text{Cu}(\text{OH})_2$, are also commonly present. When copper ends up in soil it strongly attaches to organic matter and minerals over a wide range of pH values. As a result of this, it does not travel very far after release and it hardly ever enters groundwater (28). The affinity of Cu for humates increases as pH increases and ionic strength decreases. Copper does not break down in the environment and because of that it can accumulate in plants and animals when it is found in soils. On copper-rich soils only a limited number of plants have a chance of survival. Copper can interrupt the activity in soils, as it negatively influences the activity of microorganisms and earthworms. The decomposition of organic matter may seriously slow down because of this. In anaerobic environments, when S_2 is present $\text{CuS}(\text{s})$ will form. The cupric ion (Cu^{2+}) is the most toxic species of Cu. Toxicity has also been demonstrated for CuOH^+ and $\text{Cu}_2(\text{OH})_2^{2+}$ (28, 40). Acute inhalation of Cu dust or fumes at concentration of $0.075\text{-}0.12\text{mg/m}^3$ may cause metal fume fever with symptoms such as cough, chills and muscle ache (41). The TDI for Cu based on a 10 kg child is $1400\text{ }\mu\text{g/day}$ (37) and for MDI $7000\text{ }\mu\text{g/day}$ based on a 20 kg child (38).

In plants, Cu is essential in seed production, disease resistance and regulation of water. Copper in excess can be phytotoxic to plants and it has been used as an algicide to control algal blooms. It can cause plant damage if, for example, it is present at too high concentration in sewage sludge which is applied to agricultural land. Copper is required by humans in trace level in order to help haemoglobin formation and carbohydrate metabolism

1.3.5 Nickel (Ni)

The most important oxidation state of the Ni is +2. It also exists as certain compounds in which the oxidation state of the metal is between -1 and +4. It is used in stainless steel production, nickel-cadmium batteries, alloys, and electroplating. Nickel is resistant to corrosion by air and water under ambient conditions and combines readily with other metals including Cr, Cu, Fe and Zn to form alloys (42). Nickel contamination may occurs from emissions of metal mining, smelting, and refining operations; Nickel plating and alloy

manufacturing; land disposal of sludge, and disposal of effluents. Nickel is found in the environment combined primarily with oxygen or sulphur as oxides or sulphides. Nickel is a potent skin sensitiser (that is, able to cause allergic reaction in humans) and as many as 1 – 4% of men and 8 – 20 % of women in the general population may be Ni sensitive (43). The TDI for Ni based on a 10 kg child is 500 µg/day (37) and for MDI 130 µg/day based on a 20 kg child (43). Direct contact of Ni leads to skin rash which is the most common type of reaction to Ni exposure (44). Ingestion of Ni can cause skin reactions in previously sensitised individuals. The other main concern for oral exposure to Ni is its developmental toxicity potential, which has been observed in experimental animal studies (43). Soluble Ni salts and the mixture of Ni sulphides and oxides present in refinery dust are carcinogenic to the lung and nasal tissues in humans (43). Other toxic effects of Ni observed following inhalation exposure include chronic bronchitis, emphysema, reduced vital capacity and asthma. Nickel is present in a number of enzymes in plants and microorganisms. In humans, Ni influences Fe absorption and metabolism, and may be an essential component of the haemopoietic process.

1.3.6 Lead (Pb)

The primary industrial sources of Pb contamination include metal smelting and processing, Pb battery manufacturing, pigment and chemical manufacturing and Pb contaminated wastes. Widespread contamination due to the former use of Pb in gasoline is also of concern. Lead released to groundwater, surface water and land is usually in the form of elemental Pb, lead oxides and hydroxides, and lead metal oxanion complexes (27). Lead occurs most commonly with an oxidation state of 0 or +2. Pb^{2+} is the more common and reactive form of lead and forms mononuclear and polynuclear oxides and hydroxides. Under most conditions Pb^{2+} and lead-hydroxy complexes are the most stable forms of Pb (27, 28). Low solubility compounds are formed by complexation with inorganic (Cl^- , CO_3^{2-} , SO_4^{2-} , PO_4^{3-}) and organic ligands (humic and fulvic acids, EDTA, amino acids) (28, 29). Lead carbonate solids form above pH 6 and PbS is the most stable solid when high sulphide concentrations are present under reducing conditions. Most Pb that is released to the environment is retained in the soil (45). The primary processes influencing the fate of Pb in soil include adsorption, ion exchange, precipitation, and complexation with sorbed organic matter. These processes limit the amount of Pb that can be transported into the surface water or groundwater. The relatively volatile organo lead compound tetramethyl lead may form in anaerobic sediments as a result of alkylation by microorganisms (27). The amount of dissolved Pb in surface water and

groundwater depends on pH and the concentration of dissolved salts and the types of mineral surfaces present. In surface water and ground-water systems, a significant fraction of Pb is undissolved and occurs as precipitates (PbCO_3 , Pb_2O , $\text{Pb}(\text{OH})_2$, PbSO_4), sorbed ions or surface coatings on minerals, or as suspended organic matter. Lead can be very toxic for human health. For children: reduction in intellectual quotient, hyperactivity, hearing loss. For adults: increased blood pressure; liver, kidney and fertility damage. The TDI for Pb based on a 10 kg child is 36 $\mu\text{g}/\text{day}$ (37).

1.3.7 Zinc (Zn)

Zinc is a fairly reactive metal that will combine with oxygen and other non-metals, and will react with dilute acids to release hydrogen. Zinc does not occur naturally in elemental form. It is an essential trace element which is present in soil and can be toxic when exposure exceeds physiological needs. It is usually extracted from mineral ores to form ZnO. The primary industrial use for Zn is as a corrosion-resistant coating for iron or steel (27, 28). Metallic Zn is mixed with other metals to form alloys such as brass and bronze and also used to make dry cell batteries. Zinc oxide is used in the manufacture of paints, rubber, ceramic and many other products. The main source of exposure to zinc is from food though there might be oral exposure arising from working in industries where Zn is used as source of raw materials. Zinc usually occurs in the +II oxidation state and forms complexes with a number of anions, amino acids and organic acids. Zn may precipitate as $\text{Zn}(\text{OH})_2(\text{s})$, $\text{ZnCO}_3(\text{s})$, $\text{ZnS}(\text{s})$, or $\text{Zn}(\text{CN})_2(\text{s})$. Zinc is one of the most mobile PTEs in surface waters and groundwater because it is present as soluble compounds at neutral and acidic pH values. At higher pH values, Zn can form carbonate and hydroxide complexes which control its solubility. Zinc readily precipitates under reducing conditions and in highly polluted systems when it is present at very high concentrations, and may co-precipitate with hydrous oxides of iron or manganese (27, 28). Sorption to sediments or suspended solids, including hydrous iron and manganese oxides, clay minerals, and organic matter, is the primary fate of Zn in aquatic environments. At high doses Zn may interfere with calcium metabolism and impair immune responses. The TDI for Zn based on a 10 kg child is 5000 $\mu\text{g}/\text{day}$ (37) and for MDI 27000 $\mu\text{g}/\text{day}$ based on a 20 kg child (38)

1.3.8 Platinum group elements (PGEs)

The PGEs consists of iridium (Ir), osmium (Os), palladium (Pd), platinum (Pt), rhodium (Rh) and ruthenium (Ru). These elements are all transition metals lying in the d-block (Group 8, 9

and 10 and period 5 and 6). Platinum and Pd are found in pure state in nature (46). The other four elements Ir, Os, Rh and Ru occur as alloys of Pt and Au (47). The concentration of PGEs in the lithosphere is very low, with the average estimated to be in the range of 0.001–0.005 mg/kg for Pt; 0.015 mg/kg for Pd; 0.0001 mg/kg for Rh; 0.0001 mg/kg for Ru; 0.005 mg/kg for Os; and 0.001 mg/kg for Ir (48). Of the six PGEs, the ones of interest for this study are Pd, Pt and Rh because of their use in the construction of catalytic converters used in the automobiles. Platinum group elements released from the catalytic converters are primarily bound to aluminium oxide particles (49). They were until recently, regarded as inert elements but recent studies have shown that they may be soluble and quite reactive (50). The details of PGEs are discussed in chapter six.

1.4 Contaminated Land Legislation

The legal definition of 'contaminated land', as provided by Part IIA of the Environmental Protection Act 1990 (51) is: “Land which appears to the local authority in whose area it is situated to be in such a condition, by reason of substances in, on or under the land that a) significant harm is being caused or there is a significant possibility of such harm being caused or b) pollution of controlled water is being, or is likely to be, caused”. This Act came into force in England and Scotland in 2000 and in Wales 2001. The Act creates a framework to identify and clean up contaminated land, where contamination poses unacceptable risks to human health or the environment. The UK follows a non-statutory Contaminated Land Exposure Assessment Model (CLEA) which details a standard approach in dealing with contaminated land and associated human health risk assessment for England and Wales. The approach is risk based and involves an assessment which is carried out to determine whether the land is fit for its current use or redevelopment (52). The risk assessment explores and investigates the likelihood, presence and significance of the pollutants and their linkages, which is the relationship between a contaminant, pathway, and the receptor. The concept of this linkage pathway is to assess the size of the hazards associated with the pollutants and how the source-pathway-receptor interlink with each other forming a pollutant linkage (Figure 1.1) (53) that poses potential risk to human health, eco-system and plants.

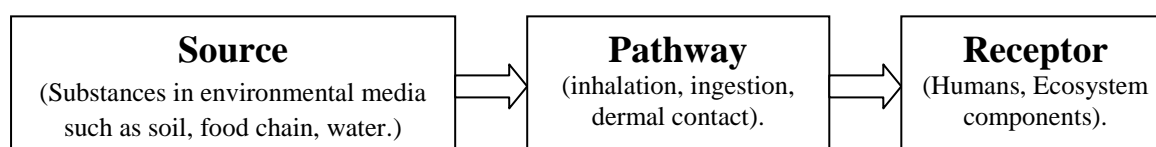


Figure 1.1: Exposure linkage of contaminant to receptor

To evaluate the degree of soil contaminant using the risk-based approach there is set guidelines by the Environmental Agency and DEFRA, Soil Guideline Values (SGV). Soil guideline values give an indication of the representative average levels of contamination in soil below which the long-term human health risks should be minimal and above it there may be a cause for concern and possibility of posing significant risk to human health. The SGV has been modelled for three main land uses: (a) residential (b) allotments and (c) commercial/industrial. They are designed to be applicable across the range of site conditions and contaminant forms that are typically encountered on the UK (54). It is a generic risk assessment criteria which can be used in the preliminary assessment of the risk to human health from chronic exposure to contaminated soil. Soil guideline values are derived using the contaminated land exposure assessment model (CLEA). The CLEA model is based on comparing predicted contaminant exposure levels with established toxicological levels (or Health Criteria Values: HCV). The basic assumption in using the CLEA model to derive SGVs is that contaminant released from the soil is taken up into the body to the same extent as from the medium or organism used to derive the HCV. In a situation where the HCV is determined using organisms other than human or contaminants are present as recalcitrant compounds, the above assumptions using CLEA model may not necessarily be true (55). At present SGVs are available for only As, Cd and Ni among the metals being studied with the rest being either recently withdrawn or not available. Generic assessment criteria published by CEIH and LQM (38) are available for a range of other metals.

1.5 Assessment of environmental risk to humans using oral bioaccessibility

There are several methods of assessing environmental risk of soil contaminants to humans. In England, DEFRA supports the use of CLEA model i.e SGVs and generic risk assessment as outlined in section 1.2. The Scottish and Northern Ireland Forum for Environmental Research (SNIFFER) proposed method for deriving site-specific human health assessment criteria for contaminants in soil and is adapted in Scotland and Northern Ireland. In all these methods, the assumption is that the total metal concentration in the soil ingested is equal to that absorbed by the body. None of these methods until very recently considered the internal exposure or dose which is the actual fraction of the total amount of ingested contaminant from the soil that reaches the systemic circulation; hence the risk from soil intake with regards to metal contamination may be overestimated.

Oral bioaccessibility can be determined by either *in vivo* or an *in vitro* method. The *in vivo* method requires direct tests with human or suitable animal models as a surrogate for humans. The use of humans for bioaccessibility testing is understandably not feasible on ethical grounds. The routine use of animals is also challenging in terms of cost, time, facilities and ethical issues (56). On the basis of the above, *in vitro* method of measuring oral bioaccessibility has been developed. The principle underlining *in vitro* methods is that uptake of a contaminant depends on the rate and extent of its dissolution in the gut (56). There are different types of *in vitro* models (57). The *in vitro* bioaccessibility test mimics the digestive system of humans by using reagents/enzymes. The digestive system of humans consists of the mouth, stomach and the small intestine. The mouth compartment of the digestive system in most of the *in vitro* methods is omitted because of the short time the contaminant spends in the mouth. The stomach and the small intestine is therefore the major compartment of the system and where the contaminant spends most of the time hence the definition of oral bioaccessibility as the fraction that is soluble in the gastrointestinal environment and available for absorption (58). The major problem facing *in vitro* method is the issue of validation, reproducibility and robustness for regulatory acceptance in risk assessment. At present, none of the *in vitro* methods has been approved by regulators in the UK and the bioaccessible fraction obtained largely depends on the applied *in vitro* method. The Bioaccessibility Research Group of Europe (BARGE) unified method (which is batch based) focuses on digestion characteristics as a method of separation was used in this work. This method has recently undergoing a unification process and it is anticipated that it should provide a standard method that will produce a conservative estimate of the oral bioaccessible fraction of contaminants from soil to be used in human health risk assessment.

In vitro bioaccessibility testing should be validated with the *in vivo* method. Unfortunately, no UK soil samples have undergone *in vivo* testing hence the true or acceptable bioaccessibility values of the metal contaminants in UK soils are still unknown.

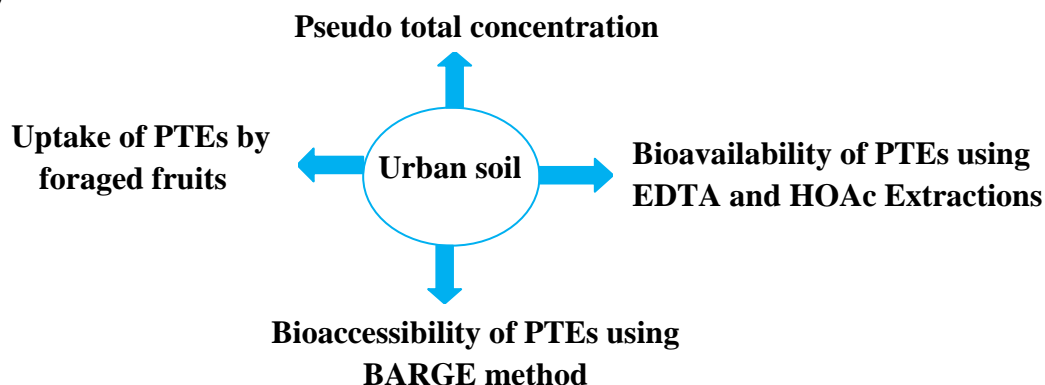
1.6 Aims and objective of the research.

An overview is shown in Figure 1.2 and highlights two main environmental media investigated: Urban soils and urban road dust. All of the experiments were designed to achieve the following aims:

- (a) Optimisation of microwave digestion (Chapter 2)

(b) To determine the pseudo total PTE concentration (using the above method) of environmental media as part of a generic quantitative risk assessment at an urban park (Chapter 3).

(i)



(ii)

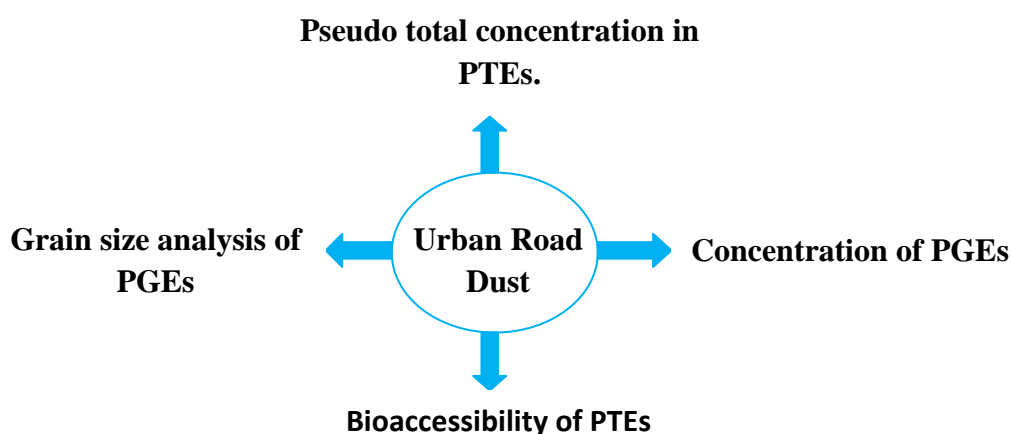


Figure 1.2: Overview of the study

- (c) To augment this study through the investigation of PTE bioavailability using EDTA and HOAc (Chapter 3).
- (d) To evaluate the application of *in vitro* oral bioaccessibility testing using the BARGE method (Chapter 4).
- (e) To investigate the natural and anthropogenic input of PTEs in urban dusts collected from the Newcastle city centre, and its environs, and bioaccessibility of PTEs in these dusts (Chapter 5).
- (f) To investigate the spatial distribution of platinum group elements (PGEs) and the effect of particle grain size on the concentration of PGEs (Chapter 6).

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Chapter Two: Instrumental methods of measuring PTEs and microwave optimisation

2.1 Introduction

In most inorganic analytical laboratories, trace element analysis is usually performed using instrumental techniques such as flame atomic absorption spectroscopy (FAAS), X-ray fluorescence spectroscopy (XRF), graphite furnace atomic absorption spectroscopy (GFAAS), inductively coupled plasma-atomic emission spectroscopy (ICP-AES), inductively coupled plasma-mass spectroscopy (ICP-MS). These analytical techniques differ in terms of sensitivity, requirements for sample preparation, sample throughput and costs of analysis. Most of the instrument is dedicated to the analysis of either a liquid or solid samples. Instruments in which solid samples are introduced directly during measurement cover with difficulty needs usually required in environmental applications such as determinations of elements at trace or ultra-trace concentrations hence the need to transform the sample into liquid form before introduction to the instrument. For the purpose of this study, three instrumental techniques will be discussed (i.e. FAAS, XRF and ICP-MS) by focussing on the principles, basic components, the mode of operations and limitations of each of these techniques drawing out the strength and weaknesses of each of the technique rather than the detailed description of the techniques.

2.1.1 Inductively Coupled Plasma Mass Spectroscopy (ICP-MS)

Principle

ICP-MS involves the dissociation of the sample (which must be in liquid form) into its constituent atoms or ions. The ions are extracted from the plasma and passed into the mass spectrometer, where they are separated based on their atomic mass-to-charge ratio by a quadrupole. The sample is pumped at 1 mL/min into a nebulizer where it is converted into a fine aerosol with Ar gas at about 1 L/min. The fine droplets of the aerosol, which represent only 1 - 2% of the sample, are separated from larger droplets using a spray chamber. The fine aerosol then emerges from the exit tube of the spray chamber and is transported into the plasma torch via a sample injector where the processes shown in Figure 2.1 take place.

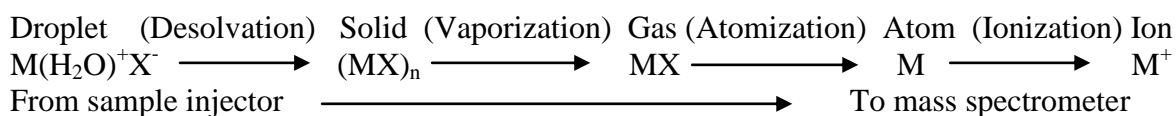


Figure 2.1: Mechanism of conversion of a droplet to positive ion in the ICP

Basic Components of ICP-MS

This is an elemental analysis technique based on production, sampling, mass filtering and detection of positive ions. There are four basic components of ICP-MS as shown in Figure 2.2.

- ❖ Inductively coupled plasma (ICP)
- ❖ Sampling interface
- ❖ Ion focusing optics and mass spectrometer (MS)
- ❖ Ion detector

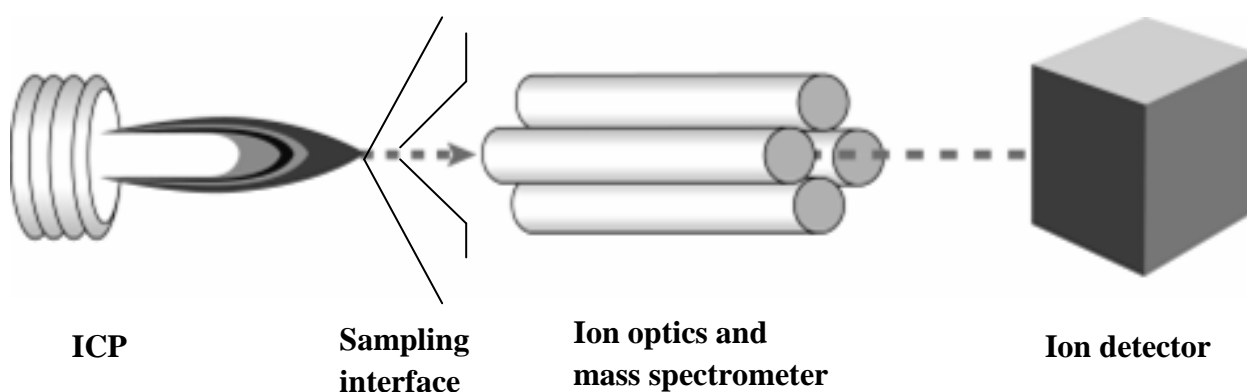


Figure 2.2: Major components of ICP-MS system (1)

ICP: This is the source of heat. The temperature ranges from 6000 -10000K (2). This high temperature is needed to dissociate (excite) the sample to form the positive ion. The process for the formation of the positive ion is shown in Figure 2.1. If the sample of interest exists as a trace metal salt in solution, the first step that takes place is desolvation of the droplet. When the water molecule is removed from the droplet, it becomes a small solid particle. As the sample moves further into the plasma, the solid particle changes first into gaseous form and then into ground-state atom. The final process of conversion of an atom to ion is achieved mainly by collisions of energetic argon electron (and to a lesser extent by argon positive ion) with the ground state atom (3). The ion then emerges from the plasma and is directed into the interface of the mass spectrometer

Sampling interface: The sampling interface lies between ICP and MS. The ICP torch which is used to ionize and atomize materials requires high operational temperature (about 7000K), while the mass spectrometer is operated at room temperature and requires the vacuum condition to avoid collisions with any gas molecules before ions can reach the detector. This task is accomplished by the use of interface between ICP and MS, and the use of vacuum

pumps to remove nearly all the gas molecules in the space between the interface and the detector.

Ion optics: The ion optics are positioned between the skimmer cone of the sampling interface and the mass separation device. The function of the ion optic system is to take ions from the hostile environment of the plasma at atmospheric pressure via the interface cones and steer them into the mass analyzer, which is under high vacuum. Another important role of the ion optic system is to stop particulates, neutral species, and photons from getting through to the mass analyzer and the detector. These species cause signal instability and contribute to background levels, which ultimately affect the performance of the system.

Mass Spectrometer: These are used to separate isotopes based on their mass to charge ratio (m/z). Three basic mass analyzer are available for ICP-MS: (i) quadrupole (ii) magnetic sector field (high resolution) and (iii) time of flight (TOF). The most common type among these is the quadrupole because of its compactness and ease of use. One of the disadvantages of the quadrupole is that it offers low resolution when dealing with ions of the same mass to charge ratio. Comparisons between the three analysers are presented in Table 2.1.

Table 2.1: Comparison of mass analysers figure of merit (4).

Parameter	ICP-QMS	ICP-SFMS	ICP-TOFMS
Sensitivity (cps)	10^5	10^6	10^3 - 10^4 per m/z
Background (cps)	1-10	<0.1	1-10 per m/z
Resolving power	Unit mass	Upto 10000	Upto 1500
Precession (% RSD)	0.1	0.05	0.02
Ion sampling mode	Sequential	Sequential	Simultaneous
Cost	£	££	£
Speed	Fast	Slow	Fast
Maintenance/operation	Easy	Complex	Easier than SFMS.
Spectral generation m/zs^{-1}	2000-3000	350	6000000 based on 300 m/z measured @20000Hz

Ion detector: The ion beam separated by the mass analyzer is converted to electrical signal using detector. The most common type of ion detector found in an ICP-MS system is the electron multiplier.

Strength and weakness of ICP-MS

The advantages of using ICP-MS for analysis of PTEs includes low detection limit (ng/l), multi element analysis, wide dynamic range, isotopic measurement, speed of analysis is very high, high productivity, very economical for many samples, easily interpreted spectra and can also be used in hybrid techniques e.g. laser ablation ICP-MS for solids and liquid

chromatography ICP-MS for speciation studies. Limitations of using the equipment include high initial capital cost, requires some method development skills, it suffers some spectral interferences and samples are limited to <0.2% dissolved solids therefore need to be properly filtered.

2.1.2 Flame Atomic Absorption Spectroscopy (FAAS)

This is a very common technique for detecting PTEs and metalloids in environmental samples. It is a reliable technique and simple to use. The technique is based on the fact that ground state PTEs absorb light at specific wavelengths. PTE ions in a solution are converted to atomic state by means of a flame. Light of the appropriate wavelength is supplied and the amount of light absorbed can be measured against a standard curve.

Principle:

The technique requires a liquid sample to be aspirated and mixed with combustible gases, such as acetylene and air or acetylene and nitrous oxide. The mixture is ignited in a flame whose temperature ranges from 2100 to 2800 °C. During combustion, atoms of the element of interest in the sample are reduced to free, unexcited ground state atoms, which absorb light at characteristic wavelengths. The characteristic wavelengths are element specific and accurate to 0.01-0.1nm (5). To provide element specific wavelengths, a light beam from a lamp whose cathode is made of the element being determined is passed through the flame. A detector (photomultiplier) detects the amount of reduction of the light intensity due to absorption by the analyte, and this can be directly related to the amount of the element in the sample.

Basic components of FAAS

Flame atomic absorption hardware is divided into six fundamental parts namely: (a) Radiation source. (b) Atom cell (c) Wavelength selector (Monochromator) (d) Detector (e) Amplifier (f) Signal processor as shown in Figure 2.3

Radiation source: The hollow cathode lamp is the most common radiation source in atomic absorption spectroscopy. The cathode is made of the element of interest with a low internal pressure of an inert gas (Ne or Ar). The hollow cathode lamp provides a constant and intense beam of analytical light line for the element of interest.

The Atomizer: The atom cell consists of two parts: the nebulizer and the flame. The

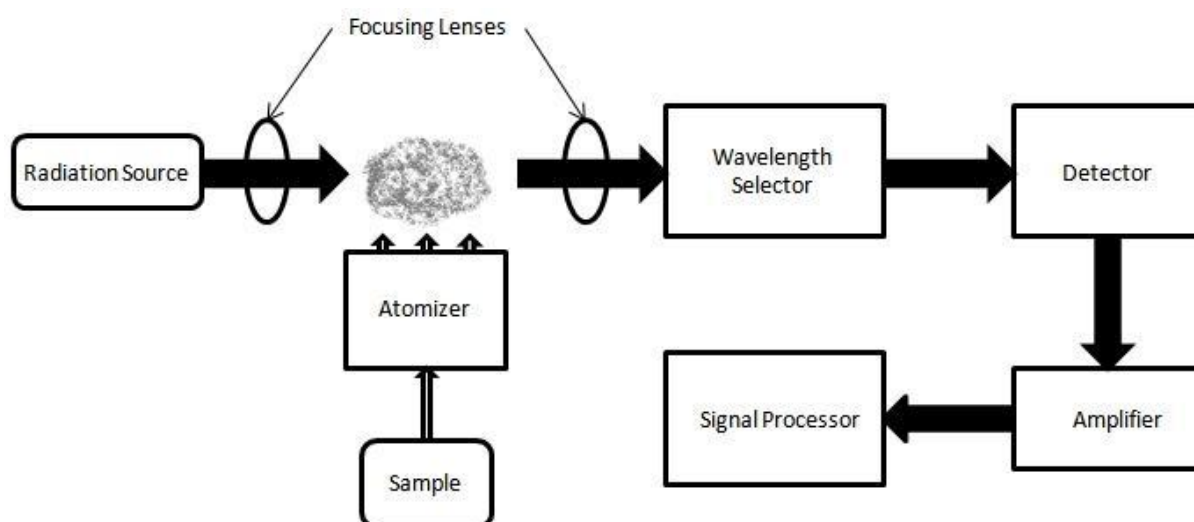


Figure 2.3: Block diagram of atomic absorption spectrometer (6).

nebulizer sucks up liquid sample at a controlled rate, create a fine aerosol, mix the aerosol and fuel and oxidant thoroughly for introduction into the flame. The flame destroys any analyte ions and break down complexes. It (flame) create atoms (the elemental form) of the element of interest example Fe^0 , Cu^0 , Zn^0 , etc

The Monochromator: This is the wavelength selector. It isolates analytical lines' photons passing through the flame and remove scattered light of other wavelengths from the flame. In doing this, only a narrow spectral line impinges on the detector.

The detector: The common detector used is the photomultiplier (PMT), the function of which is to convert the light signal into an electrical signal. The processing of electrical signal is fulfilled by a signal amplifier. The signal could be displayed for readout or further fed into a data station for printout by the requested format.

Strength and weakness of FAAS: The strengths of using FAAS includes relatively few interference, good performance, robust interface, low capital cost, being fast and easy to use. However, FAAS has moderate detection limit ranging from $\mu\text{g/l}$ and mg/l , It has element limitation i.e. can be used to measure metals only, only one element per determination, the instrument has no screening ability and cannot be used for isotopic measurement.

2.1.3 X-ray Fluorescence (XRF)

In both environmental studies and quality control processes, it is of significance that the analytical procedures used for elemental determination should be rapid and simple, taking

into account the number of samples to be analyzed. Atomic spectroscopy, including FAAS and ICP-MS are common techniques used for PTE determination in environmental samples (7, 8). However, these techniques require a prior destruction of the matrix by mineral acids which may lead to problems of contaminants by reactants employed or disturbances of the measured concentration by element losses due to incomplete solubilization and/or evaporation (9, 8). Moreover, the method of matrix destruction used strongly depends on the chemical composition of the sample and on the element to be determined (10). In view of these problems, the use of other methods for direct and multi-elemental analysis of samples has been increasing over the last few years, including X-ray fluorescence spectrometry (XRF) (11). Simplicity of sample preparation, minimum manipulation, speed, cost effectiveness, application to a wide range of concentrations from 100% to few part per million (ppm) and the chance of analyzing some elements such as sulphur that can hardly be determined by other techniques have promoted XRF as a useful alternative to conventional spectroscopic techniques.

Principle

In XRF Spectrometry, high-energy primary X-ray photons are emitted from a source (X-ray tube) and strike the sample. The primary photons from the X-ray tube have enough energy to knock electrons out of the innermost, K or L, shell. When this occurs, the atoms become ions, which are unstable. An electron from an outer shell, L or M, will move into the newly vacant space at the inner shell to regain stability. As the electron from the outer shell moves into the inner shell space, it emits an energy known as a secondary X-ray photon. This phenomenon is called fluorescence. The secondary X-ray produced is characteristic of a specific element. The energy (E) of the emitted fluorescent X-ray photon is determined by the difference in energies between the initial and final shell of the individual transitions. This is described by equation 2.1

$$E = hc/\lambda \quad 2.1$$

Where h is Planck's constant; c is the velocity of light; and λ is the characteristic wavelength of the photon. Energies are inversely proportional to the wavelengths; they are characteristic for each element.

Basic components of XRF

The setup of XRF instrumentation (Figure 2.4) consists of four basic components (a) An

excitation source (b) A sample (c) A detector (d) A data collection and analyzing system. The excitation source is typically an x-ray tube. The x-ray tube sends a beam of x-rays with various energies to the sample, and the sample absorbs and emits the x-rays to the detector. The detector senses each impinging x-ray and sends electrical pulses to the data collection and analyzing system. The analyzing system categorizes each x-ray by its energy. This set up is a generic one. The X-LAB 2000 instrument used in the present study incorporates secondary targets and polarisation of sample excitation X-ray. The polarisation drastically reduces the scattering background in the collected spectrum resulting in improved limits of detection and reduced measurement times. Three Barkla scatterer targets are used for this purpose; boron carbide which is optimised for elements from manganese to molybdenum; aluminium oxide optimised for trace element analysis for the elements from molybdenum to cerium; highly ordered pyrolytic graphite for other elements. Secondary targets enable optimal excitation of the element from potassium to manganese, independent from the iron content of the sample (12).

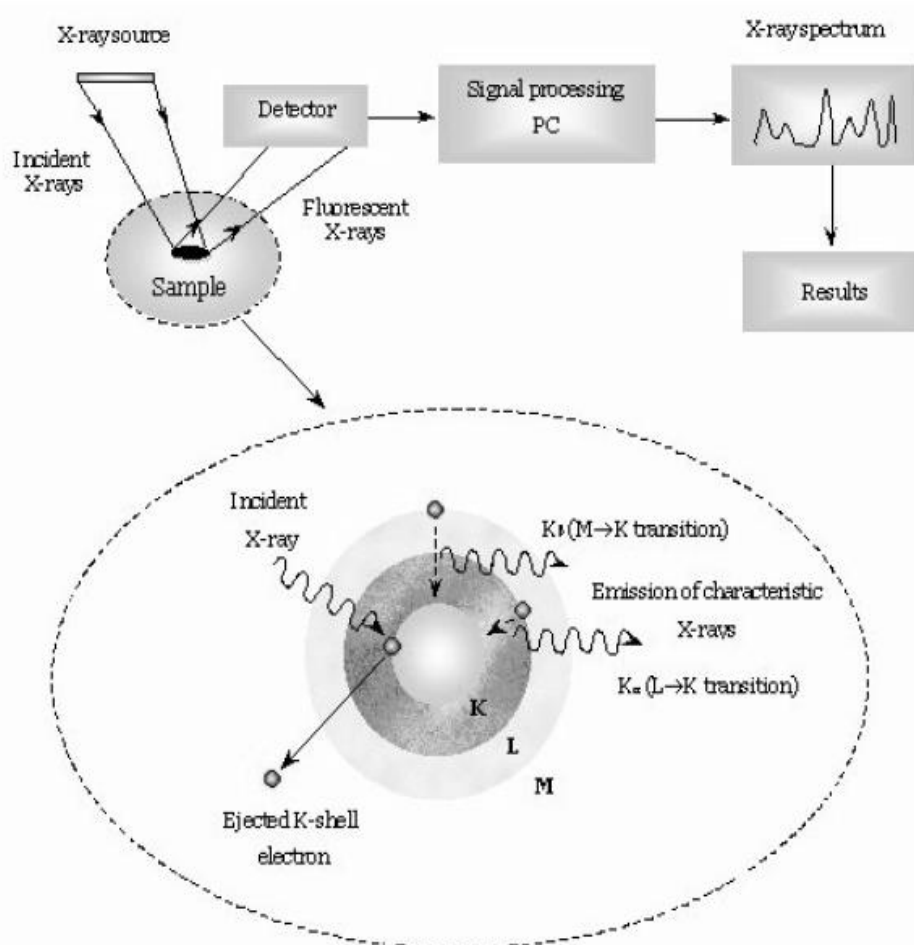


Figure 2.4: The principle of XRF and the typical XRF detection arrangement (13)

Strength and weakness of XRF: The strengths of XRF have already been alighted in section 2.1.3.. The major weakness of XRF is that analyses are generally restricted to elements heavier than fluorine. It has limited sensitivity for some important pollutant elements (e.g., Cd and Pb) and a somewhat poorer precision and accuracy compared to atomic spectroscopic techniques (14). In addition the detection limits of ICP-MS and FAAS are better than those of XRF and the latter is also not suitable for isotopic measurement. Comparison of the three techniques is shown in Table 2.2

Table 2.2: Comparison of Elemental Techniques

Parameters	XRF	FAAS	ICP-MS	References
Detection limits	% - ppm	mg/l	ng/l	15, 16
Sample throughput		10-15 secs per element	All elements in <1minute	17
Dynamic range	Wide	10 ³	10 ⁸	16
Interferences	Very few	Few	High	18
Dissolved solids in solution	N/A	0.5 -5%	0.1-0.4	16
Sample volume required	Very large (g)	Large	Very small	16
Isotopic analysis	No	No	Yes	7
Ease of use	Very easy	Easy	Moderately easy	16
Method development	Very easy	Easy	Difficult	16, 19
Capital cost	Very low	Low	Very high	15, 16
Sensitivity	Good	High	Very high	15
Sample preparation method	Non destructive	Destructive	Destructive	20, 14, 21

2.2 Principal sources of uncertainty in environmental trace analysis.

Figure 2.5 show that chemical analysis of environmental samples can be divided into the following steps: planning, representative sampling, preparation of the samples, instrumental measurement of the analytical signal and evaluation of the data. Generally each step in the analysis contains an uncertainty.

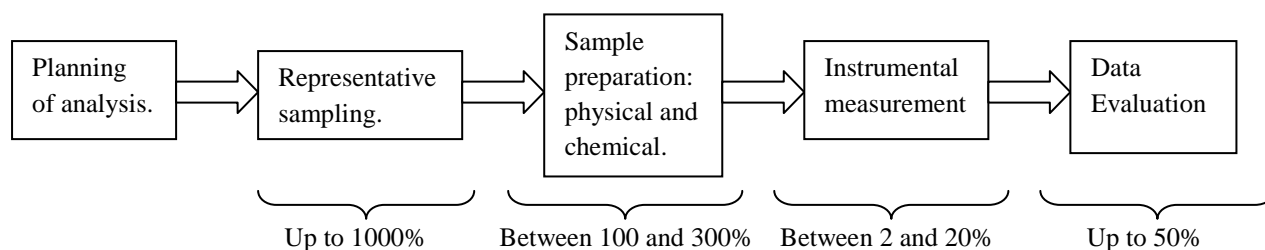


Figure 2.5: Flow chart for inorganic environmental analysis including a rough error estimation of the different analytical procedure (16).

In any analytical investigation the degree of difficulty and the likelihood of error depend less on the physico-chemical properties of the substance or sample to be analyzed than on the

concentration range in which the substance to be determined occurs in the sample (4).

Whereas % and ppm ranges can often be determined without much trouble and as a matter of routine, at ppb and even more at ppt levels present a problem.

2.2.1 Sample preparation

In the analysis of environmental samples, one of the most common sources of error which analysts encounter are those emanating from preparation steps. Sample preparation is the most critical part of the analysis because it is responsible for the most and often hidden sources of errors. It is usually time-consuming and many errors influencing the reliability of the final results may be introduced at this stage (22). Errors due to contaminations may be usually overcome if necessary precautions are taken concerning reagents, equipment and the manner of working. Contaminations, frequently observed, are due to systematic or random introduction of non-negligible amounts of the analyte during different steps of the analysis. The choice of the sample preparation procedure will depend on the measurement technique used. Sample preparation involves several stages. For solid samples, the stages includes drying (air, laboratory oven 39 to 42°C), homogenization (mixing/crushing), grinding (mills, mortars), followed by a sub sampling, mineralization and dissolution of a subsample. Most of these steps performed in the laboratory may be sources of contaminations, essentially due to the type of vessels and purity of reagents, used. Drying protects the sample material against microbial decomposition during subsequent storage and acquires constant reference value by determining the dry weight as opposed to the fresh weight, which is difficult to quantify. Samples that cannot be dried immediately can be kept in a refrigerator at 4°C before being processed further (23). To obtain a representative sample and increase the surface area of the sample, the solid sample has to be split into smaller parts by applying a mechanical force. The size of the sample is reduced further by grinding. Grinding generally applied to solid samples prior to the dissolution procedure, may contaminate the sample by abrasion of the mortar or milling parts with certain hardness (24). Sample preparation steps necessitate the use of reagents and vessels made in porcelain, glass, quartz, PTFE, platinum or various plastics. Impurities present in reagents are important (and often systematic) sources of contaminations, in particular if they are added in great amounts. Total dissolution of samples cannot be achieved in one step using a single reagent. In practice, a number of steps and reagents is dictated by the matrix composition. The dissolution process can lead to volatilization of the analyte arising from high temperature (eg dry ashing) or volatilization of

chlorine ions as nitrosyl chloride (NOCl) as in acid digestion, adsorption, coprecipitation of the analyte with a precipitate formed by a main matrix element within the reactive mixture (2). Incomplete dissolution as a result of wrong choice of reagent can lead to error. The good choice of the sample preparation procedure, the quality of its application and a suitable laboratory environment become therefore the most critical points for a successful trace element analysis.

The matrix of a sample is responsible for the degree of difficulties encountered during analyses because it will impose constraints not only in the analyte determination but also during preparation steps (8). In view of elevated concentrations of analyte, the sample matrix is the factor responsible for interference observed during measurements of other elements present at lower concentrations.

Samples collected for environmental monitoring fall into different categories as a function of the analytical difficulty associated to the complexity of the matrix and/or concentration levels to determine: Waters (drinking, surface, ground, and rain); Soils, sediments, suspended particulate matter collected in natural waters, dusts; Plant samples; Seawater (ultra-trace concentrations), biological fluids (very complex matrix: blood, milk, or highly variable matrix: urine); Wastes (urban or industrial) (8). Depending on the instrument for measurement, the sample can be introduced either in solid or liquid form. Very few techniques allow solid samples to be introduced directly into the instrument for analysis therefore analysis of solid samples by other methods involve bringing them into a solution in order to satisfy needs of introduction systems of most analytical techniques utilized in routine laboratories.

2.2.2 Sample collection and storage

Sampling is the first and one of the most important steps, in analysis and has the role of ensuring the representativity of the sample in the context studied. For this reason also, it represents the most potential source of errors. A representative sample is one that is evenly distributed, and is required for the analysis. One of the special problems of environmental analysis is that the quantity of the original sample may be in kilogramme or tonne range and out of this only a few hundred milligrams can be put into the equipment for the actual analysis (7). In other words, there is very considerable reduction in bulk from the original

sample to the sample used for measurement. Nevertheless, it has to be ensured that the sample used in analysis has the same mean chemical composition as the original sample. Depending on the samples to analyze and elements to be determined, the sampling tools, filtration devices and storage vessels have to be carefully chosen and cleaned to minimize risks of possible contamination (22). All vessels to be used should thus be washed, rinsed and then soaked overnight in 1–10% (v/v) analytical grade nitric acid. Finally, before use all vessels should be rinsed in high purity deionised water. Sample collection and storage is associated with the risk of contamination especially when the sampling is to do with low concentration of the analyte (8). In order to minimize analyte losses by adsorption of metal ions on the vessel or on the suspended particles, the samples collected can be stored for a short time in a refrigerator, and for longer periods in a freezer. For the same purpose, aqueous solutions are generally acidified immediately after sampling (generally at pH 1.5 with nitric acid) (16). This treatment is generally sufficient to prevent the adsorption of trace elements on to walls of the vessel for relatively long term storage. Another means to avoid adsorption losses is immediate freezing of the sample collected and its thawing just before measurements. This is the best method for storage of natural waters because an acidification may mobilize into solution some trace elements associated with particulate matter present in the sample.

2.3 Optimisation of microwave digestion

Acid digestion or wet decomposition is routinely employed for the determination of elements in solids in order to transfer the analytes into solution so that they can be introduced into the instrumentation (e.g. ICP-MS, AAS) in liquid form (25, 26). Acid digestion involves the use of acid and heat to destroy the organic matrix, carbonate bound fractions and sorbed fractions of a sample to liberate the metal content. It measures the total or pseudo-total (depending on the reagent used for the digestion) concentration of the metal present in the sample matrix. In this study, acid digestion was carried out using aqua regia ($\text{HCl}:\text{HNO}_3$ 3:1 v/v) and microwave system to heat the sample. Microwave radiation is a non-ionising radiation in the frequency range of 300 and 300,000 MHz (27). The frequency of 2450 MHz is used throughout in every microwave oven apparatus (27, 28). The interaction between sample and microwave radiation is due to two processes (29, 30). The first process is the dipole rotation as a function of the oscillating electromagnetic field. At 2450 MHz, the dipole aligns and randomises five billion times a second. In the second process the ionic conduction

mechanism takes place whereby the ionic species migrate in the direction of the electric field. These two processes produce intense heating which is faster than the convection and thermal conduction used in classical heating methods. Thus, heating efficiency depends on the presence of polar molecules (e.g. water) and ions in the sample environment. High temperatures can be reached at relatively low pressures (31, 32). Microwave digestion is therefore a rapid and efficient method of sample decomposition prior to determination of trace metals. The advantages of microwave digestion involve higher recovery of the analyte, shorter extraction time and use of smaller quantities of solvent (33, 34). A large number of different acid mixtures have been used for microwave digestion e.g. HNO_3/HCl , $\text{HNO}_3/\text{H}_2\text{SO}_4$, $\text{HNO}_3/\text{HClO}_4$ and sometimes HF. In this work, an acid mixture of HCl/HNO_3 (3:1 v/v) was used and the degree of dissolution during microwave digestion was examined by investigating four variables, namely acid volume (V), digestion time (t), microwave power input (P) and temperature (T). The optimised conditions of these variables were used in the digestion of soil reference material and its concentration determined to ascertain the accuracy of the method

2.4 Experimental.

2.4.1 Central Composite Design (CCD).

Central composite design (CCD) is required in order to establish the optimum conditions and also to obtain information about the inter-relationships between the variables (35). A central composite randomised design was set up to obtain the various reaction conditions for each run. Twenty eight standard runs were obtained from the CCD. Each of the variables had limits set at five coded levels: $-\alpha$, -1, 0, +1 and $+\alpha$ (36). The variables identified were temperature, time, power and volume of solvent. The use of a CCD allows all operating parameters to be investigated individually, as squared terms, and to consider interaction effects (36). The results of the CCD were evaluated using multilinear regression. The range of metals for which this technique has been applied are Cr, Cu, Ni, Pb and Zn. Table 2.3 shows the minimum and maximum values for each of the variables which were employed to generate the equation of a straight line used in the computation of the various values for each run. The experimental design for the 28 standard runs using the four variables was set up and is shown in Table 2.4. To fully understand the way in which microwave system affects digestion, individual operating variables were considered along with nonlinear effects and interaction terms. The operating variables were studied using a full second order central

composite design (36). The results from the central composite design can be assessed using multilinear regression represented by equation 2.2

$$Y = \beta_0 + \beta_1 T + \beta_2 t + \beta_3 P + \beta_4 V + \beta_5 T^2 + \beta_6 t^2 + \beta_7 P^2 + \beta_8 V^2 + \beta_9 T.t + \beta_{10} T.P + \beta_{11} T.V + \beta_{12} t.P + \beta_{13} t.V + \beta_{14} P.V \quad (2.2)$$

Where T = Temperature, t = time, P = Power, V = Volume, β_0 = Intercept and $\beta_1 - \beta_{14}$ = Parametric coefficients and Y = Response

Table 2.3: Upper and lower limit of the variables for computing conditions for standard runs

Variables	Temperature (T°C)	Time (t) minutes	Microwave power (P) Watts	Volume (V) mL of acid mixture
+2.27519	80	10	550	10
0	130	20	675	13
-2.27519	180	30	800	16
-1	160	24	730	14
+1	110	16	620	12

2.4.2 Instrument and Reagents

All chemicals used were of analytical grade. Concentrated HCl and concentrated HNO₃ were obtained from Fisher Scientific UK. Ltd. (Loughborough, Leicestershire). A multi-element standard containing Cr, Cu, Ni, Pb and Zn and internal standard solution containing Sc, In, and Tb were purchased from SPEXCertPrep (Middlesex, UK). Ultra pure water of conductivity 18.2MΩ-cm was produced by a direct Q™ millipore system (Molsheim, France). A soil certified reference material (GBW 07401) from China (Certified 1986, Revised 1998) was used. ICP-MS measurements were carried out with an ICP mass spectrometer X series II (Thermo Electron Corporation, Cheshire, UK.). All digestions were carried out using a Start D multiprep 42 high throughput rotor microwave digestion system supplied by Milestone Microwave Laboratory Systems UK. The weighing balance used was Explorer Ohaus model E406 00032 from Switzerland.

2.4.3 Microwave digestion protocol

The Start D microwave system has a sample capacity of 42, maximum temperature of 200 °C with a PFA vessel of volume 65 mL. 0.5 g of the soil sample was weighed into the vessel pre-cleaned with an acid (Conc. HNO₃). Then different volumes of aqua regia (HCl:HNO₃ 3:1

v/v) depending on the standard run were added to the soil. The vessel was sealed with the TFM cover. The sealed vessels were placed inside a rotor of the microwave digestion system and submitted to a microwave dissolution program shown in Table 2.6. Ventilation (cooling) time of 30 minutes was allowed while the vessels were still in the oven.

Table 2.4: Experimental design which shows the range of conditions for the variables

Standard run	Temperature (°C)	Time (minutes)	Power (W)	Volume (mL)
13	110	16	730	12
10	110	24	620	12
26	130	20	675	16
8	160	16	620	14
2	160	24	620	14
5	160	25	730	14
19	80	20	625	13
21	130	10	625	13
25	130	20	550	13
18	180	20	675	13
16	110	16	620	12
3	160	25	750	13
1	160	24	730	12
23	130	20	675	13
14	110	16	620	14
12	110	24	620	14
7	160	16	730	12
15	110	16	730	14
24	130	20	800	13
28	130	20	675	13
11	110	25	730	12
6	160	16	620	12
17	130	20	675	13
4	160	24	620	12
9	110	24	730	14
27	130	20	675	10
22	130	20	675	13

After cooling, the digest was filtered using a whatman filter paper into a 50 mL volumetric flask and diluted to the mark with Milli-Q water of conductivity 18.2MΩ-cm at 25 °C. For each digestion, reagent blanks were also carried out. The blanks were prepared in the same way as the sample except that the sample was not added in the blank. The filtrate obtained from the digestion was stored in the fridge (4 °C) prior to metal analysis.

2.4.4 ICP-MS protocol

An X series II ICP-MS was tuned using a 10 ng/l solution of Li, Be, Bi, Ce, Co, In, Ba, Pb, Tl, U in 2% HNO₃ to verify mass resolution (37, 38). The tuning was done in standard and CCT (Collision Cell Technology) mode. The CCT mode is used for the first order transition elements. The conditions for standard mode and CCT mode are shown in Table 2.5.

Calibration standards of 0-400 ng/l prepared from a 100 mg/l stock solution of the multi element mixture were used to calibrate the instrument. The soil samples were diluted with an appropriate dilution factor. A mixed internal standard (Sc, In and Tl) was added to the diluted soil samples, calibration standards and blanks and all analysed using ICP-MS.

Table 2.5: Operating conditions for ICP-MS

ICP-MS Conditions	Standard Mode	CCT Mode
Extraction	-152.9	-156.9
Forward Power (W)	1400	1400
D1	-40	-40
D2	-140	-110
Quadrupole Bias (V)	0.2	-14
Hexapole Bias (V)	-2.0	-18
Nebuliser gas flow (L/min)	0.83	0.83
Count rate	⁷ Li>40000, ¹¹⁵ In>200000,	⁵⁹ Co>10000, ¹¹⁵ In>50000,
Ratio Limit	¹⁵⁶ CeO/ ¹⁴⁰ Ce<0.0200	¹⁵⁶ CeO/ ¹⁴⁰ Ce<0.0200
Collision cell gas (L/min)	N/A	H ₂ /He (4.50)
Cool gas flow (L/min)	13.0	13.0
Auxiliary gas flow (L/min)	0.90	0.90
Internal standards	⁴⁵ Sc, ¹¹⁵ In, ¹⁵⁹ Tb	⁴⁵ Sc, ¹¹⁵ In, ¹⁵⁹ Tb

2.5 Results and Discussion

2.5.1 Microwave Optimisation

The calibration data and the total PTE concentration in a selected local soil sample is shown in tables 2.6 and 2.7 respectively. The individual PTEs in Table 2.6 are investigated using a multilinear regression equation (equation 2.2). Statistical treatment of these data is shown in Table 2.8. It is clear that some individual PTE have statistical significance at the 95% confidence level (p value < 0.05) as summarised in Table 2.9. From the statistics, temperature, time and power play significant role in the digestion process. Temperature and power play a significant role in Cu dissolution while the dissolution of Zn has time as the major factor as shown by the statistical analysis. This can be demonstrated by considering

temperature and power for Cu recovery. At the highest power of 800 watts and a moderate temperature of 130 °C (Standard run 24), the Cu recovery is 208.4 mg/kg while keeping the time constant at 20 minutes and volume of 13 mL. This recovery is very close to the highest value of Cu obtained in all the runs (the optimised run). At the highest temperature of 180 °C and power of 675 watts (Standard run 18), Cu recovery is 168 mg/kg at constant time and volume of 20 minutes and 13 mL respectively though not too close to the optimum value but goes a long way in showing that the majority of the dissolution in this case comes more from temperature than from power. Similarly, the recovery for Zn is poor (418 mg/kg) when the lowest time of 10 minutes was applied in the digestion (standard run 21). At other lower t of 16 minutes, the recovery varies depending on the temperature, power and volume of solvent used. Example standard run 7 had Zn recovery of 759 mg/kg when a time of 16 minutes is used. The temperature used for the dissolution is 160 °C and the power is 730 watts which is high enough to produce such a reasonable recovery in 16 minutes. The highest recovery of Pb (506.7 to 659.9 mg/kg) occurs mainly between the temperatures of 130 to 160 °C (Standard runs 25, 3, 24, 17 and 7). For a constant t of 20 minutes, volume of 13 mL and temperature of 130 °C, the recovery for Pb for runs 25, 24 and 17 are 506.7, 522.8 and 556.0 mg/kg respectively while the high temperature of 160 °C for time of 25 minutes and also volume of 13 mL for standard run 3 gave 659.9 mg/kg. Though the standard run 7 was operated at high temperature of 160 °C the recovery for Pb in this run is lower than that of run 3 because the time of operation (16 minutes) was lower. Standard run 3 gave the highest recovery in all of the elements (Cr, Cu, Ni, Pb and Zn) studied. The optimised values are 97.0, 250.5, 98.9, 659.9 and 998.3 mg/kg for Cr, Cu, Ni, Pb and Zn respectively (Table 2.7). The optimised conditions that gave the optimum values are temperature of 160 °C, a time of 25 minutes, power of 750 watts and a volume of 13 mL (standard run 3). These conditions were used in the microwave digestion of subsequent samples. In comparison with literatures, it is observed that the microwave conditions vary depending on the mass of the sample used in the digestion and the manufacturer / model of the microwave. For instance Navarro et al., 2008 (39) used a Start D model with 0.3 g mass of sample and conditions were 500 W for 10 minutes and 450 W for 18 minutes making a total of 28 minutes for the digestion and the volume of aqua regia used was 15 mL while operating at a temperature of 160°C. Yasemin et al., 2007 (40) used a Perkin Elmer Multiwave 3000 with 0.5 g mass of sample with a power of 600 W, digestion time of 30 minutes and aqua regia volume of 12 mL. Nouri et al., 2007 (41) used a 0.1 g mass of sample in two microwave models: ETHOS and MARS 5

microwave systems. In the ETHOS system the conditions used were 12 mL of aqua regia, 60 minutes digestion time, 650 W power and an operating temperature of 220 °C while in the MARS 5 the conditions were 3 mL of aqua regia, digestion time of 15.5 minutes operating at a power of 600 W and temperature of 175°C. These variations identify the importance of optimising the microwave instrument before being used in the digestion of real samples.

Considering the fact that only Cu and Zn show statistical significance at 95% confidence, stepwise linear regression may be a more appropriate technique to use for the microwave optimisation study.

Table 2.6: ICP-MS calibration data for PTEs Cr, Cu, Ni, Pb and Zn.

Elements	Isotope	Calibration Equation $y = mx + c$		Correlation Coefficient r^2	
		Standard Mode	CCT Mode	Standard Mode	CCT Mode
Cr	^{52}Cr	$y = 1461.9x + 12.1$	$y = 587.6x + 10.9$	0.9998	0.9997
Cu	^{63}Cu	$y = 1020.9x + 11.9$	$y = 681.6x + 5.8$	0.9994	0.9993
Ni	^{60}Ni	$y = 378.9x + 35.6$	$y = 235.4x + 3.4$	0.9998	0.9996
Pb	^{208}Pb	$y = 82677x + 0.8$	N/A	0.9993	N/A
Zn	^{66}Zn	$y = 2798.5x + 6.4$	$y = 2772.5x + 6.5$	0.9996	0.9995

2.5.2 ICP-MS Analysis of soil CRM

In order to assess the accuracy and precision of the optimised microwave digestion followed by ICP-MS or FAAS protocol soil certified reference materials (GBW 07401 from China) was analysed. The results, shown in Table 2.10 show good agreement between the certified and measured values. The ICP-MS measurement was conducted in both standard and collision cell technology (CCT) modes. The CCT mode is used mainly for first order transition elements to reduce oxide formation. The obtained results and the percentage recovery (shown in brackets) for the total metal analysis are shown in Table 2.10. From the result, Cr has a measured value of 62.9 mg/kg in standard mode and 61.5 mg/kg in CCT mode with 102% recovery in standard mode and 99% in CCT mode. The standard deviation for Cr in standard mode is ± 2.3 and ± 0.5 for CCT mode. The results in both modes are good but Cr was measured in CCT mode in the sample because of a smaller standard deviation obtained when the CRM was measured. The measured values for Ni, Cu and Zn in CCT mode are also closer to the certificate value compared to the standard mode. The percentage recovery obtained from CCT mode in these elements are all above 95% compared to the

Table 2.7: Concentration of PTEs measured by ICP-MS in Ouseburn soil samples

Std Run	Cr mg/kg	Cu mg/kg	Ni mg/kg	Pb mg/kg	Zn mg/kg
16	51.5	189.1	75.4	382.7	636.0
10	50.2	170.9	74.7	360.7	554.3
13	47.5	163.7	68.8	348.6	595.6
20	64.6	176.8	79.5	399.2	635.2
19	49.2	195.3	77.4	391.8	822.5
18	81.3	168.0	78.2	453.7	635.5
5	90.7	187.9	85.5	447.7	635.5
2	83.2	163.8	90.3	405.7	664.5
8	74.2	157.4	84.6	385.5	586.3
21	67.9	222.1	92.7	372.4	418.0
25	97.5	196.7	92.1	506.7	817.0
26	69.7	207.0	95.4	493.2	972.7
1	72.6	158.2	85.4	434.5	662.5
3	97.0	250.5	98.9	659.9	998.3
28	61.3	182.8	92.2	391.4	663.0
12	53.8	167.4	86.1	368.7	597.5
15	55.2	173.0	84.9	391.8	595.6
6	65.8	167.4	78.9	392.8	605.3
11	49.1	171.8	75.4	378.8	661.9
4	68.1	245.8	85.9	389.6	603.7
24	67.5	208.4	93.2	522.8	710.7
14	54.7	241.7	82.7	493.0	569.5
9	53.7	195.0	77.8	427.0	767.0
27	58.6	203.0	81.9	498.0	747.0
17	58.4	207.0	88.0	556.0	738.0
7	74.0	205.0	94.0	555.0	759.0
23	56.0	159.0	84.0	392.0	614.0
22	72.0	198.0	77.0	458.0	701.0

standard mode whose recoveries are < 90% except for Zn. Zinc in standard mode gave a recovery of 97% and concentration of 660.9 mg/kg compared to CCT mode which gave 101% recovery and 688 mg/kg concentration. Zn was measured in CCT mode for the sample because the measured value (688 mg/kg) for the total metal concentration is closer to the certificate value (680 mg/kg) than in standard mode (660.9 mg/kg). The recovery is also higher in CCT mode than in the standard mode for Zn. Pb is measured in standard mode. The result for Pb showed 96 mg/kg for measured value and 98 % recovery compared to the certificate value of 98 mg/kg. On the basis of the elements determined in the soil CRM,

Table 2.8: Statistical treatment of individual PTE data using multilinear regression

Parameter	Variable	Ni		Cr		Cu		Zn		Pb	
		Coeff	P	Coeff	p value	Coeff	p value	Coeff	p value	Coeff	p value
β_0		601.3614	0.2333	1475.9270	0.0948	-1596.0525	0.2718	-1612.9	0.7379	-2922.112	0.6533
β_1	T	-0.1711	0.9033	-4.1746	0.0995	7.0057	0.1031	14.9881	0.2889	29.3234	0.1324
β_2	t	-16.1548	0.0965	-26.0584	0.1135	-2.8772	0.9138	-216.084	0.0296	-89.6912	0.4650
β_3	P	-0.7228	0.3542	-2.0115	0.1405	1.4758	0.5095	9.0154	0.2437	4.8505	0.6338
β_4	V	-14.8792	0.6679	-27.9420	0.6364	126.0447	0.2209	57.1615	0.8662	113.4817	0.8039
β_5	T²	0.0013	0.1887	-0.0008	0.6083	-0.0012	0.6551	-0.0051	0.5798	-0.0073	0.5485
β_6	t²	0.0891	0.1876	0.0535	0.6324	-0.1714	0.3717	0.9547	0.1527	-0.9683	0.2734
β_7	P²	5.18E-05	0.9014	-4.5E-05	0.9495	-0.0001	0.9173	-0.0083	0.0597	-0.0104	0.0769
β_8	V²	-0.7569	0.3039	-2.0290	0.1158	-4.4109	0.0503	-12.876	0.0862	-18.8807	0.0644
β_9	T.t	-0.0008	0.9663	0.0023	0.9427	-0.0204	0.7103	0.1768	0.3500	-0.1073	0.6695
β_{10}	T.P	-9.59E-05	0.9446	0.0043	0.0848	-0.0099	0.0247	-0.0266	0.0662	-0.0173	0.3503
β_{11}	T.V	-0.0078	0.9181	0.1068	0.4132	0.0303	0.8897	0.1268	0.8644	-0.9058	0.3724
β_{12}	t.P	0.0095	0.2843	0.0230	0.1372	0.0232	0.3652	0.1415	0.1150	0.1622	0.1742
β_{13}	t.V	0.5067	0.3002	0.5705	0.4883	-0.1117	0.9357	5.2106	0.2785	2.7640	0.6634
β_{14}	P.V	0.0362	0.3088	0.0808	0.1882	-0.0243	0.8098	0.2205	0.5219	0.6331	0.1842

Table 2.9: PTEs statistically significant at 95 % confidence interval

Metal	Variable of significance
Cu	T.P
Zn	t

the following operating modes were identified as the most appropriate. Cr, Cu, Ni, Zn would be determined in CCT mode while Pb will be determined using standard mode. All future soil samples were measured using these experimentally determined ICP-MS operating mode conditions.

Table 2.10: Total PTE concentration in soil CRM GBW 07401 by ICP-MS/FAAS

Element	GBW 07401 (Soil)		
	Certificate Value Mean \pm SD (mg/kg)	Measured Value (mg/kg)	
		Mean \pm SD (n = 3)	
		Standard Mode	CCT Mode
As	34 \pm 5	NA	34.8 \pm 5.4
Cd	4.3 \pm 0.6	4.8 \pm 1.2	NA
Cr	62 \pm 6	62.9 \pm 2.3 (102)	61.5 \pm 0.5 (99)
Cu	21 \pm 2	14.9 \pm 1.8 (71)	20.0 \pm 2.3 (96)
Ni	20.4 \pm 2.7	15.7 \pm 2 (77)	20.1 \pm 2.9 (102)
Pb	98 \pm 8	96 \pm 2 (98)	NA
Zn	680 \pm 39	660.9 \pm 3 (97)	682 \pm 10 (100)
Pb~	98 \pm 8	99.3 \pm 0.1 (101)	
Zn~	680 \pm 39	688 \pm 7 (101)	

~ Measured by FAAS, NA = not available, Nos in brackets are % recoveries.

In all, the elements determined using the optimised condition gave good result when compared with the certificate values hence the validity of the method. Note that Zn and Pb were also measured in the CRM (Table 2.10) using FAAS because some of the soils collected across the study site were of such high concentration to warrant the use of FAAS rather than ICP-MS (see chapter three). From the results the recovery/accuracy in each case is 101%.

2.6 Conclusion

The type of instrument needed to carry out PTEs analysis is dependent on the nature of the sample, the analyte concentration and the sensitivity of the instrument. The optimised microwave condition obtained in this work is temperature of 160°C, time of 25 minutes, volume of the aqua regia of 13 mL and power of 750 watts. These optimised conditions are used in subsequent analysis.

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Chapter Three: Evaluation of PTE contamination at a former industrial site (St Anthony's Lead Work) in Newcastle upon Tyne

3.1 Introduction

PTEs are well-known for their toxic effects and therefore information on their concentrations and distribution in the environment is important. Pollution of the environment by these elements can pose a serious threat to plants, animals and even human beings because of bioaccumulation, non-biodegradable properties and toxicity of the contaminants even at low concentrations. Since these elements are non-biodegradable, their pollution is long lasting.

Different approaches are used for soil and sediment analysis, many of them focussed on pollutant desorption from the solid phase; others on the pollutant adsorption from a solution by the solid phase. Among the approaches based on desorption, leaching procedures are the most widely accepted and used (1). Leaching involves two processes: - (a) Mobilization of the target metal from the solid particle and (b) Dissolution of metal-containing solid phases (e.g. Al, Fe, Mn oxides or hydroxides, organic matter and silicate minerals). The dissolution process is a three step mechanism involving (1) fast ligand adsorption onto surface functional groups of solid particles (2) slow mineral metal detachment and (3) fast protonation restoring the original surface functional groups (2, 3). Changes in environmental conditions, whether natural or anthropological, can strongly influence the behaviour of both essential and potentially toxic elements by altering the forms in which they occur. The transfers of metals from soil to plants pose potential health risks because they can enter the food chain and the environment (4). Plant uptake is one of the major pathways by which heavy metals enter the food chain (5, 6). The uptake of PTEs by plants from soils is of interest because excess dietary intakes are detrimental to human health.

Of the leaching extraction processes, single and sequential extraction has been the most widely accepted and used. Sequential extraction provides more detailed information about the different availabilities of PTEs partitioning among different geochemical phases, enabling differentiation between several physical forms of speciation: exchangeable, carbonates, oxide, organic-bound and residual forms. The most widely used method for determining sequential extraction are those proposed by Tessier et al. 1979 (7) and modified by Rauret et al. 1999 (8). The former method has four steps, where four fractions of extractable PTEs are released from the sample:- exchangeable (ion exchange PTEs), associated with carbonates (acid soluble PTEs), associated with Fe-Mn oxides (reducible PTEs) and associated with

organic matter (oxidizable PTEs) (9). The modified method constitutes three steps, with the major difference to Tessier et al. 1979 method being the replacement of the first two steps with a single step, use of large sample size and an increase in the volume of extractant (10). In both cases, the residual fraction is always digested using aqua regia and summed up with those of other fractions and compared with the result of a separate aqua regia digest of the whole soil (pseudo total). This is an additional step. The conventional protocol of the Tessier et al. 1979 method, or its modification, is a time consuming procedure owing to the lengthy operating time required in the successive extraction steps and consequently, could be considered tedious for routine analysis especially when considering the bioavailable fraction, hence the use of single extraction (9).

Single step extractions are mainly applied to soil samples to identify the bioavailable fraction using a number of different reagents to extract all, or part of, the metals from soil. A commonly used single extraction approach to characterise soil bioavailable fraction of metals is the use of the HOAc/EDTA procedure (11). Using EDTA to extract metals has been proven to be effective because of its strong complexing ability (11). The advantages of EDTA in heavy metal extraction are high efficiency of metal extraction, formation of metal complexes which are thermodynamically stable and soluble, low adsorption of the chelating agents and their metal complexes on soil (12-14). According to Perez et al. 2002 (9), single extraction procedures provided similar amounts of extractable PTEs to those released in the first three fractions of the Tessier et al. 1979 method, which can be considered to be the more mobilizable fractions. Laboratory studies have shown that EDTA is effective in mobilising PTEs (15).

The determination of PTEs in foraged or edible fruits is not well reported in the literature. Exceptions, for example, include studies on the PTE content of blackberries (16, 17), wild berries (18) and (tropical) fruits (19). As the potential human health risk from gathering foraged fruits is unpredictable (a) due to seasonal variation (excess and low abundance) and (b) an individual's intention to gather, the need to assess this source of contamination has importance. The growing public awareness of potential contaminants in foodstuffs, coupled with the growth in farmers markets selling 'home-made' produce e.g. jams and natural herbal remedies, raises concerns about the source of such produce especially foraged fruits and berries from former industrial sites. In this study foraged samples from a former industrial site, now used as a local community countryside park, present a potential human health risk

either from direct consumption of fresh samples or following their conversion in to products for private consumption or sale e.g. jam. Of particular importance on this site is the presence of Pb (20); however other elements were also analysed in the foraged fruits (As, Cd, Cr, Cu, Ni and Zn).

This work is aimed at (1) evaluating the pseudo- total PTEs content at the site (the former St Anthony's Lead works) (2) comparing the effectiveness of HOAc and EDTA in the extraction of PTEs from the site. (3) to evaluate the soil-to-plant transfer factors (gathered over two successive sampling seasons) for predicting a potential health risk from forage fruits once soil contamination levels are known.

3.1.1 Site description

The St Anthony's Lead Works was situated along the banks of the river Tyne to the South-east of Newcastle City Centre. The area of the site is about 52,651 m². The factory which operated from around 1840 to mid 1930s smelted lead ore imported from Europe, mainly Spain and processed this along with United Kingdom produced lead (20). The factory refined lead ore to extract silver and then manufactured *white* and *red* lead, and made sheet and lead pipe. The site was landscaped in the mid 1960s (20). Current uses of the site include:- fishing on the riverside, ball games, walking, and dog exercise. The site is currently occupied by Walker Riverside Park. and site surfaces include hard standing (footpath, road and car park) grassed and shrubby/wooded areas (Table 3.1). Figure 3.1 shows the period usage where the soil samples were collected and Figure 3.2 the site layout where the foraged samples were collected.

Table 3.1: Site Description of former St Anthony's lead works (20)

Description of location.	The site is situated next to both Felling View and Pottery Bank in the Walker area of Newcastle.
Site Boundaries.	North- Disused railway track, East- Pottery Bank, South- River Tyne, West- Open ground.
Site Setting	The site is situated on the banks of the River Tyne in a predominantly recreational area and consists of public open space.
Adjacent Land Uses	Adjacent land uses includes educational, recreational and residential.
Site Surfaces	This include hard standing (footpaths, car park and road) grassed, landscaped and planted areas
Vegetation	Vegetation present on the site includes grassed areas, shrubs and trees.
Subsurface Structures	This may include foundations, structures and various tanks associated with the sites former land uses.

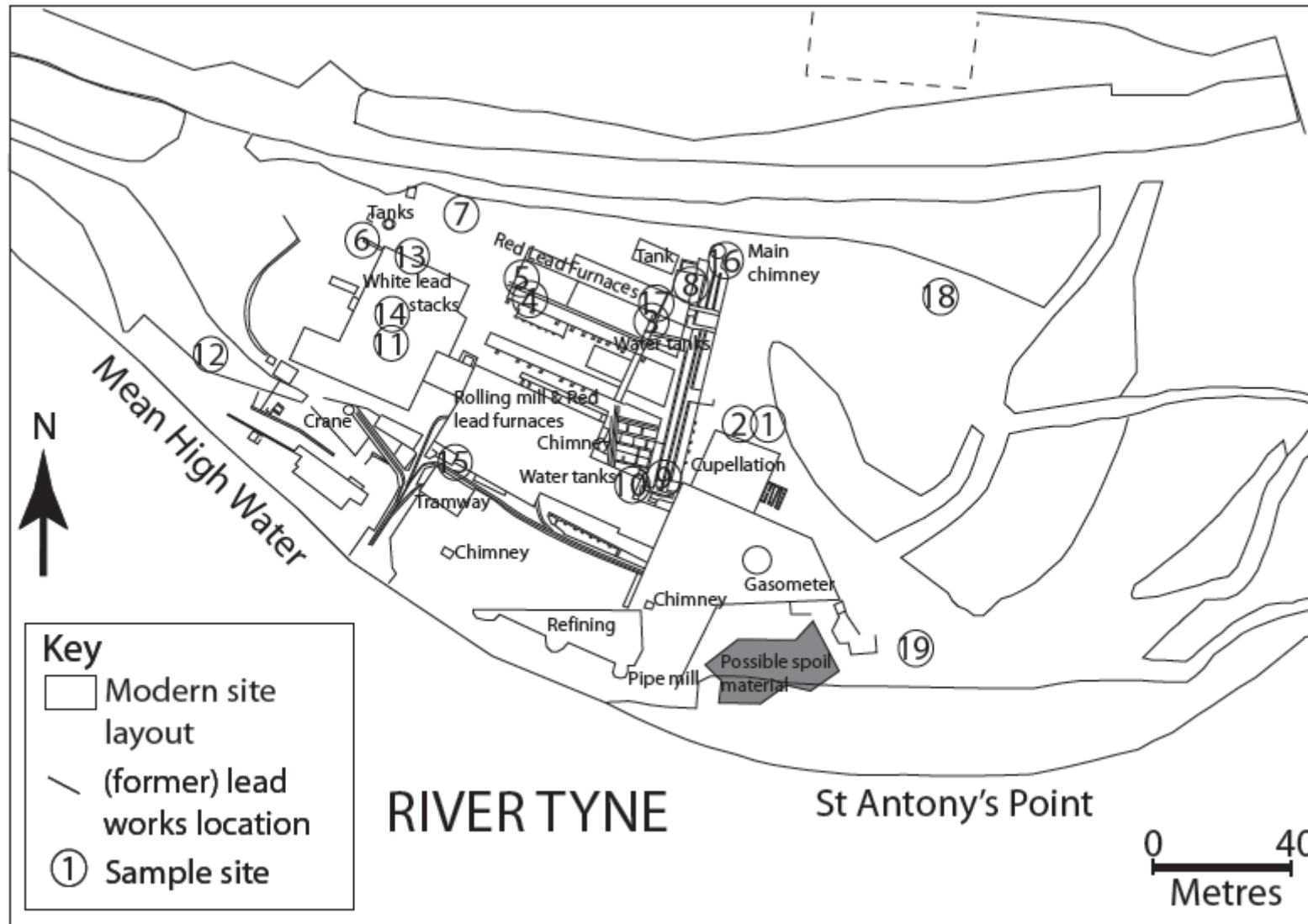


Figure 3.1 Sample locations for soil samples at former St Anthonys lead site. The building are labelled to indicate previous usage.

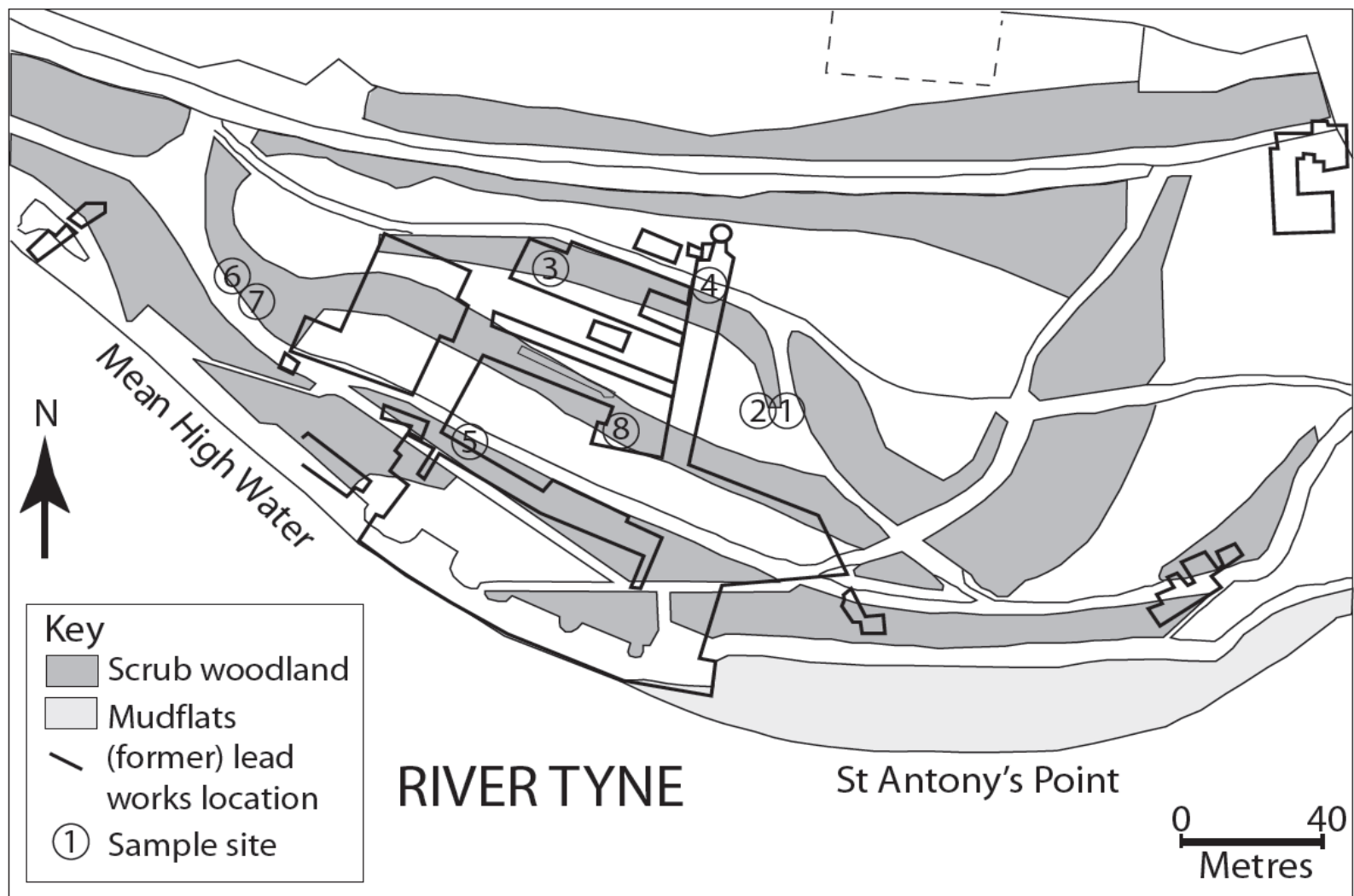


Figure 3.2 Sample locations for foraged fruits collected from former St Anthonys lead works. The layout of the former buildings and infrastructure are also indicated.

3.2 Experimental

3.2.1 Sampling and sample preparation

Samples of soil were collected from 19 sample points on the site (Figure 3.1) by digging a square hole of about 10 cm² from the top soil. The grass on the top of the soil was removed. The top soil collected was put inside a wax paper geochemical bag, and labelled to include the sample point, date of collection and the site where it was collected. The hole created was covered back after the collection. During sampling, sample handling and sample preparation polyethylene gloves were worn. The soil samples were dried in the sample bags in an oven at a temperature of <40°C for 6 days. The dried soil samples were gently disaggregated in a porcelain pestle and mortar and passed through a plastic sieve of mesh size 2 mm and stored. A powdered sub-sample was digested using microwave digestion technique and then stored in the fridge for metal analysis using ICP-MS and FAAS. The description of the sample site is shown in Table 3.2

Also samples of foraged fruit (blackberry, elderberry, rosehip and sloes) were collected from the site over two successive seasons (September 2007 and 2008; Figure 3.2). In terms of sample size per site a minimum of 10 fruits were collected for blackberry, sloes and rosehips, whereas for elderberry a plethora of berries was collected. Immediately following collection, all samples were washed thoroughly in distilled water and the edible portions prepared for analysis. This involved oven drying of samples at a temperature of 37°C for about 28 days, followed by powdering using an agate mortar and pestle.

3.2.2 Instrument and Reagents

In addition to the instrument and reagents used in 2.2.2, EDTA from BDH chemicals Ltd Poole England and HOAc from Fisher Scientific UK Ltd (Loughborough, Leicestershire) were used. Carbolite AAF 1100 furnace was used in organic matter content determination. All pH were measured using a Jenway 3020 pH meter supplied by S.H scientific Blyth Northumberland UK. Soil mixing was done using SB3 rotator by Stuart (end over end). Flame atomic absorption spectroscopy (FAAS) measurements were carried out using an A. Analyst model 100 supplied by Perkin Elmer Corporation, Norwalk, Connecticut, USA. Energy dispersive X- ray

Table 3.2: Description of sampling site & sample.

Sample No	Description of sampling site	Description of sample
SAL 1	Open grassy area (recently mown), c 50cm from trees.	Topsoil (imported) sample 1-10 cm
SAL 2	Near foot of the slope dominated by scrub woodland (principally Elder, Hawthorn & Rosehip at sample location). Approx. 50 cm from sample 1 and just into the undergrowth (scrub).	Removal of overlying litter layer. Topsoil (made ground/imported soil) just under trees/shrubs sampled 0-10cm.
SAL 3	Base of slope dominated by scrub woodland (principally shrubs & Silver Birch at sample location), near visible occurrences of red lead.	Removal of overlying litter layer. Topsoil (made ground) under trees/shrubs sample 0-10cm.
SAL 4	Open grassy area (recently mown), approx. 20 cm from rough grass fringing the slope. Near utilities cover.	Topsoil (imported) sample 1-10cm.
SAL 5	Sample taken from wooded (scrub) slope.	Removal of overlying litter layer. Topsoil (made ground) sample 0-10cm.
SAL 6	Collected at apex of short slope in open (bare) ground adjacent to trees/shrubs.	Topsoil (made ground) sample 0-10cm.
SAL 7	Rough grass/herbs.	Topsoil (imported) sample 1-10cm.
SAL 8	Adjacent to tarmac path at top of steep slope, next to fence.	Topsoil (made ground) sample 1-10cm.
SAL 9	West of cupellation near foot of slope and underneath scrub (Birch, Hawthorn, Rowan).	Litter layer removed. Topsoil (made ground) sample 0-10cm.
SAL 10	Grassy area near edge of scrub covered slope.	Topsoil (imported) sample 1-10cm.
SAL 11	Open grassy area (recently mown), approx. c 50cm from scrub woodland.	Topsoil (imported) sample 1-10cm.
SAL 12	Steep wooded slope	Top soil 0-10 cm.

SAL 13	Ashy slope. Unofficial path.	Sample contains very little organics. 10 cm max. topsoil depth.
SAL 14	Steep wooded slope.	Ashy, little topsoil. Little organic matter. Furnace slag
SAL 15	Steep wooded slope.	Ashy material exposed around rabbit/fox holes. Demolition material, stone and bricks present.
SAL 16	Grass cover.	Clayey soil, with ash, bricks & stones present. Chimney area.
SAL 17	Steep wooded escarpment.	Red lead present at surface. Shallow humus/soil over clayey subsoil. Sample from top 10 cm.
SAL 18	Grass cover	Top soil (imported) sample 1-10 cm.
SAL 19	Wooded riparian slope	Sandy material. Possible presence of red lead. Possibly tipped material.

fluorescence spectroscopy (ED-XRF) analysis was performed on a Spectro Analytical X-Lab 2000 instrument fitted with a Gresham Si (Li) detector. Flame photometer used was from Evans Electroselenium LTD, Essex, UK. Carbolite AAF 1100 furnace was used in % loss of ignition (LOI) determination. An end-over-end shaker (Stuart Rotator SB3) was used for the single extraction (Barloworld Scientific Ltd., Staffordshire, UK).

3.2.3 Soil pH

The pH was determined in a soil: deionised water suspension 1: 2.5 w/v (21) as follows; 10 g of soil sample was accurately weighed into a 50 mL Sarstedt extraction tube. 25 mL of deionised water was added to the soil. The sample was placed on a shaker and agitated at 30 rpm for 10 minutes. Then, the sample was left to stand for 10 minutes and the pH recorded. The pH was measured using pH meter after being calibrated with buffer solutions of pH 4 and 7.

3.2.4 Soil organic matter content

Soil organic matter content was determined using the method of LOI as described by Baize 1993 (22). 5 g of soil sample was accurately weighed into a pre-weighed crucible. The weight of soil (W) and the weight of soil and crucible (W_1) were recorded. The sample was placed in a pre-heated muffle furnace (400 °C) for 4 hours and then cooled in a desiccator. The sample was re-weighed and the weight was recorded (W_2). The % LOI was calculated using equation 3.1.

$$\% \text{ LOI} = \frac{W_1 - W_2}{W} \times 100 \quad 3.1$$

3.2.5 Cation exchange capacity (CEC)

Soil testing laboratories do not provide direct measurement of CEC rather an estimate of it based on exchangeable cations. Effective CEC as a preferred nomenclature was determined according to the procedure described by Robertson *et al.*, 1999 (23). It involves measurement of exchangeable cations which include both the base cations (K^+ , Ca^{2+} , Mg^{2+} , and Na^+) and the acid cation (H^+). Other cations such as NH_4^+ and trace metals are usually present in minor amounts and can be effectively ignored.

Base cations measurement

4 g sample of fresh sieved soil was weighed into a 50 mL Sarstedt extraction tube. 40 mL of 1 M NH₄OAc, pH 7.0 (77.1 g NH₄OAc was added to 950 mL deionised water, adjusted pH to 7.0 with HOAc or aqueous ammonia, and made up the volume to 1.0 L with deionised water) was added to the sample. The sample was agitated on a shaker at 30 rpm for 1 hr, after which it was centrifuged at 1000 g for 10 minutes. The supernatant was removed and filtered through a Whatman No.41 filter paper for analysis using Flame Atomic Absorption Spectrometer (FAAS) for Ca²⁺/Mg²⁺ and a Flame Photometer for Na⁺/K⁺. The base cations were calculated from equations 3.2 and 3.3.

Gravimetric basis – Element mass

$$\text{mg element / kg soil} = \frac{(C \times V)}{W} \quad 3.2.$$

Where

C = concentration of ion in extract in mg/L, V = volume of extractant

W = dry mass of soil.

Gravimetric basis – Element moles of charge

$$\text{cmol}_c \text{ element / kg} = \frac{(C_g \times n)}{(10 \times A)} \quad 3.3$$

Where

C_g = element mass on gravimetric basis, as mg element /kg soil

n = valence of ion, A = atomic mass of ion

Exchangeable acidity

10 g sample of fresh sieved soil was weighed into a 100 mL extraction tube. 25 mL of 1 M KCl was added to the sample. The sample was shaken thoroughly and was allowed to sit for 30 minutes after which it was sieved in a 2 mm mesh size. The moisture content of a separate sub sample was determined as detailed in 3.2.4. The sieved solution was filtered through a Buchner funnel and the residue washed with five successive 25 mL aliquot of 1 M KCl for a total of 150 mL KCl per soil sample. To the filtrate was added five drops of phenolphthalein and titrated with 0.1 M NaOH

to the first permanent pink end point and the volume of NaOH used recorded. Five drops of phenolphthalein was added to a blank solution of 150 mL 1 M KCl passed through a Buchner funnel and titrated with 0.1 M NaOH. The volume of NaOH used was for the blank was recorded. The exchangeable acidity was calculated using equation 3.4.

$$\text{Exchangeable acidity (cmol/kg)} = (\text{NaOH}_{\text{dif}}/W) \times (0.1 \text{ mmol H}^+/\text{mL NaOH}) \times (0.1 \text{ cmol H}^+/\text{mmol H}^+) \times 10^3 \text{ g soil/kg soil} \quad 3.4$$

Where

NaOH_{dif} = mL of NaOH added to sample filtrate less mL of NaOH added to blank solution

W = g dry soil (i.e. 10 g – water content).

The effective cation exchange capacity is determined using equation 3.5

$$\text{CEC (cmol}_c / \text{kg)} = \text{exch K}^+ + \text{exch Ca}^{2+} + \text{exch Mg}^{2+} + \text{exch Na}^+ + \text{exch acidity} \quad 3.5$$

Where exch K^+ etc. = concentrations of individual ions expressed as cmolc / kg dry soil

3.2.6 Pseudo total PTE content of soil from former St Anthony's lead works

The soil samples were digested using the procedure detailed in 2.4.3. The optimised conditions of temperature of 160°C, time 25 minutes, power 750 watts and volume of 13 mL was used in the digestion process. The ICP-MS was tuned by the procedure described in 2.4.4 and the tuning conditions as shown in Table 2.5 of 2.4.4 for both CCT and Standard mode. The calibration equation is shown in Table 3.3. Lead and Zn were analysed using FAAS by preparing calibration standard from 1000 mg/kg of the stock solution. The concentration of the metal (Pb and Zn) were measured at $\lambda = 217$ and 398.8 nm, respectively.

3.2.7 Total PTE content in foraged fruits by ED-XRF

Approximately 4 g of the dried ground sample was accurately weighed and mixed with 0.65 g of Hoechst wax HWC binder. The mixture was made homogenous by

Table 3.3: Calibration Data As, Cd, Cr, Cu and Ni on ICP-MS and Pb, Zn on FAAS

Element	Isotope	Calibration Equation $y = mx + c$		Correlation Coefficient r^2	
		CCT mode	Standard mode	CCT Mode	Standard Mode
As	⁷⁵ As	$y = 562.15x + 0.02$	$y = 2952.40x - 0.04$	0.9992	0.9991
Cd	¹¹¹ Cd	N/A	$y = 435.64x + 11.15$	N/A	0.9996
Cr	⁵² Cr	$y = 587.68x + 10.97$	$y = 1461.92x + 12.14$	0.9997	0.9998
Cu	⁶³ Cu	$y = 681.63x + 5.83$	$y = 1020.88x + 11.99$	0.9993	0.9994
Ni	⁶⁰ Ni	$y = 235.42x + 3.44$	$y = 378.93x + 35.58$	0.9996	0.9998
*Pb	²⁰⁸ Pb	N/A	$y = 0.0136x - 0.003$	N/A	0.9993
*Zn	⁶⁶ Zn	N/A	$y = -0.0065x^2 + 0.136x + 0.0029$	N/A	0.9996

***Elements measured using FAAS**

shaking in a Retsch MM 200 shaker for 3 mins at 30 cycles per second. The homogenous mixture was packed in a stainless steel compartment and then formed in to a 32 mm pellet using a hydraulic press (Graseby Specac) by applying a pressure of < 10 bar. The pressed pellet was placed inside the ED-XRF instrument and its elemental composition determined

3.2.8 Single extraction using EDTA

0.05 M EDTA was prepared as ammonium salt solution by adding in a beaker 14.61 g EDTA to 80 mL deionised water. The dissolution was achieved by gradually adding 13 mL of ammonia solution (25%). The solution was then transferred to a 1.0 L Polyethylene container and approximately 900 mL of deionised water was added. The pH of the solution was adjusted to 7.0 by adding a few drops of NH_3 or HCl as appropriate and the solution was made up to 1.0 L with deionised water. 2 g of soil CRM (BCR 700) was weighed into a 50 mL centrifuge tube and 20 mL of 0.05 M EDTA (pH 7.0) was added. The mixture obtained was shaken in an end-over-end shaker at 30 rpm for 1 hr at room temperature. The mixture was centrifuged for 10 minutes at 3000 g and the supernatant was decanted, filtered through a Whatman No 41 filter paper and stored in a polyethylene bottle at 4°C. The extract was analysed using ICP-MS. The same procedure was adopted on the samples.

3.2.9 Single extraction using HOAc

0.43 M HOAc was prepared by adding 25 mL glacial HOAc to about 500mL of deionised water in a 1.0 L polyethylene container. The solution was then made up to 1.0 L with deionised water. 20 mL of 0.43 M HOAc was added to 0.5 g of soil CRM (BCR 700) in a 50 mL centrifuge tube and the mixture extracted by shaking with an end-over-end shaker at 30 rpm for 16 hrs at ambient temperature (overnight) making sure that there was no delay between the addition of the extractant solution and the beginning of the shaking. The mixture was centrifuged for 10 minutes at 3000 g and the supernatant was decanted and filtered through a Whatman no 41 filter paper and stored in a polyethylene bottle at 4°C until analysis with ICP-MS. This procedure was applied to the samples.

3.3 Results and Discussion

3.3.1 Soil properties (pH, % LOI, CEC)

The behaviour of heavy metals varies for different types of soil and so characterising the soil sample is important. Table 3.4 shows the properties of the soil collected from former St Anthony's lead works. The soil characteristics such as pH, % LOI and CEC have a direct influence on the mobility and availability of PTEs (24-27).

Soil pH is one of the most important factors in the control of the absorption, mobility and bioavailability of PTEs in the soil solution (27). A high pH contributes to a decrease of PTE mobility by the formation of precipitates, which increases the number of adsorption sites and decreases the competition of H^+ for adsorption, thereby increasing the PTE stability with humic substance. The pH was carried out in water. The average pH measurement in the sampled points from the site is 7.3

There is only limited variability in the % LOI except with that of SAL 18 where the % LOI is much higher. The average % LOI is 11.47%. The % LOI contributes to the soil CEC and a high value of % LOI results in a high value of CEC, which will have direct impact on the availability of metals.

CEC indicates the number of cation exchange sites and the value gives an idea of the number of cation adsorption sites in the soil (23). PTEs in soils of low CEC are more susceptible to leaching. Table 3.5 shows the typical CEC values for different soils. From Table 3.5, it can be seen that the CEC values at former St Anthony's lead works (SAL) (Table 3.4) falls within the normal range, except for SAL 18, which has a high value of 161 cmol/kg. The cation adsorption potential of PTEs in this case will be high because of the high CEC. According to Cameron, (28) CEC values are considered low if below 12 cmol/kg.

3.3.2 ICP-MS of soil CRM

The soil certified reference material (BCR 700) was analysed in two different modes (Standard and CCT) using inductively coupled plasma mass spectrometer (ICP-MS) for both HOAc and EDTA extraction. The results obtained are shown in Table 3.6. As noted previously, the CRM was run to check the accuracy and precision of the instrument. The CRM was run three times for each extractant (for a precision estimate) and the mean taken. The result of the CRM showed good agreement

Table 3.4: Soil Properties at St Anthony's Lead Works (SAL)

Sample Points	pH	(%) LOI	CEC (cmol/Kg)
SAL 1	6.6	10.1	14.4
SAL 2	7.5	10.9	21.4
SAL 3	7.2	10.7	19.0
SAL 4	6.6	13.0	18.5
SAL 5	7.4	11.5	19.1
SAL 6	6.5	9.1	9.4
SAL 7	6.6	16.1	-
SAL 8	7.7	14.6	-
SAL 9	7.7	11.6	27.5
SAL 10	7.6	9.4	19.7
SAL 11	7.4	7.5	24.6
SAL 12	7.7	8.2	21.7
SAL 13	7.0	10.6	22.4
SAL 14	7.9	9.6	25.8
SAL 15	8.0	8.4	23.5
SAL 16	6.9	10.7	18.0
SAL 17	7.1	15.1	21.8
SAL 18	8.1	24.7	161.0
SAL 19	7.8	6.4	18.8
Mean Values	7.3	11.5	28.6

Table 3.5: Typical CEC values for different soils (29)

Rating	CEC (cmol/Kg)	Comment
Very low	0 – 10	Very low nutrient holding capacity indicating sandy soils with little or no clay or organic matter. Nutrients will easily be leached.
Slightly low	10 -15	Slightly low nutrient holding capacity indicating a more loamy mineral soil. Nutrients will still be leached.
Normal range	15 – 40	Adequate to high nutrient holding capacity indicating soils with <u>increasing clay content</u> .
High	+ 40	Very high level normally found in very heavy soil with a high clay content or soils with a high organic matter level. Nutrients can be bound very tightly to the soil particles and therefore unavailable.

with the certificate values for both modes but the CCT mode was chosen for Cr, Cu, Ni and Zn because it gave a better accuracy than the standard mode while Cd and Pb was measured in standard mode.. All subsequent measurements with respect to single extraction determination were made using these conditions.

3.3.3 Pseudo-total PTE content of soil from former St Anthony's lead works

The range of contaminant concentration depends on the activities, disposal patterns and the nature of the soil. The specific type of PTE contamination found in former St Anthony's lead works is directly related to the operations that occurred at the site. In a typical uncontaminated soil the PTEs likely to exist in soil is shown in Table 3.7.

The pseudo-total PTE concentration of the soil from the site is shown in Table 3.8 and the box plot representation of this data (Figure 3.3) shows that Pb, Zn and As have the highest concentrations. The box plot shows that As, Cd, Cr and Zn have outliers while Pb with great variation has no outlier.

In spite of the remediation landscaping works at the site, the levels of Pb in all the sample is far above a typical soil concentration (Table 3.7) and also above the withdrawn Pb SGV (except SAL 1 and 11) for industrial/commercial which is 750 mg/kg (30). The values for Zn are well below the generic assessment criteria (GAC) value of 188000 mg/kg for industrial (31). With respect to Cd and Ni, the SGV for

Table 3.6: Single Extraction for BCR 700

Element	HOAc Extraction			EDTA Extraction		
	Certificate Value (mg/kg)	Standard Mode (mg/kg)	CCT Mode (mg/kg)	Certificate Value (mg/kg)	Standard Mode (mg/kg)	CCT Mode (mg/kg)
Cd	67.5 ± 2.8	67.5 ± 0.5 (100)	N/A	65.2 ± 3.5	63.5 ± 0.3 (97.4)	N/A
Cr	19.0 ± 1.1	16.7 ± 2.7 (87.9)	19.8 ± 0.8 (104)	10.1 ± 0.9	7.9 ± 4.2 (78.2)	10.0 ± 0.3 (100)
Cu	36.3 ± 1.6	35.5 ± 1.9 (97.8)	36.4 ± 1.1 (100)	89.4 ± 2.8	78.5 ± 3.0 (87.8)	87.9 ± 0.9 (98.3)
Ni	99.0 ± 5.1	87.9 ± 2.4 (88.8)	97.7 ± 0.8 (98.7)	53.2 ± 2.8	43.4 ± 0.8 (81.6)	61.0 ± 0.6 (115)
Pb	4.85 ± 0.38	4.6 ± 1.8 (94.8)	N/A	103 ± 5	108 ± 0.7 (105)	N/A
Zn	719 ± 24	648 ± 3.3 (90)	696 ± 1.1 (96.8)	510 ± 17	471 ± 0.7 (92.4)	498 ± 0.7 (105)
Pb~	4.85 ± 0.38	5.01 ± 0.5 (103)		103 ± 5	105 ± 3.2 (102)	
Zn~	719 ± 24	701 ± 4.5 (97.5)		510 ± 17	503 ± 24 (98.6)	

~ Measured by FAAS; N/A = Not applicable; Numbers in bracket represents % recovery

industrial/commercial are 230 and 1800 mg/kg respectively, these metals have their concentrations below the SGV. SAL 1 and SAL 11 represent the imported soil brought in as part of the remediation and landscaping process and are covered with grass (Table 3.2.)

Analysis of the data using principle component (PCA) allows simplification of the dataset to produce a new reduced set of variables known as components. Table 3.9 shows that the first two components are significant and account for 83.4%. Factor 1 accounts for 61.4% of the total variance and is dominated by Cu, Pb and Zn. Factor 2 is dominated by As and Cd accounting for 22.1% the total variance. A biplot of the first two components clearly

Table 3.7: PTEs concentration in rural soil with no local PTE input mg/kg dry soil (32).

PTE	Typical soil Concentration
Arsenic (As)	2 – 20
Cadmium (Cd)	0.1 – 1.0
Chromium (Cr)	10 – 50
Copper (Cu)	5 – 20
Nickel (Ni)	10 – 50
Lead (Pb)	0.1 – 20
Zinc (Zn)	10 – 50

separates the soils data into two main groups as shown in Figure 3.4. The interpretation of each of the components is achieved by examining the relationship between the components and the component loading. Loadings with high correlations are shown in bold and suggests PC1 summarises general PTE contamination at the site (particularly Cu, Pb and Zn) while PC2 summarises PTE contamination for As and Cd in particular. The negative loading of cluster group 1 on PC 1 reflects less contaminated sites while the positive loadings of cluster group 2 on PC 1 reflect samples with higher metal contamination. Cluster group 2 forms a more dispersed group of samples with samples 19 and 15 forming the extremes on the basis of their component loadings. Samples with high PTE concentrations (PCA cluster group 2) all come from relatively steeply sloping land some of which is bare ground (e.g. sample 13 and 6) while the majority is covered by scrub woodland. Several of the sample sites within cluster group 2 also had observable red lead deposits visible in the immediate vicinity (e.g. samples 3 and 17) and are associated with the suspected location of water tanks (sample 3) and red Pb furnaces (sample 17). All the samples taken from the open grassy area (SAL 1, 4 and 11) indicated lower elemental concentrations.

Table 3.8:Pseudo-total PTE concentration of soil from former St Anthony’s lead works

Site	Measured value in mg/kg (mean \pm SD n = 3)						
	As	Cd	Cr	Cu	Ni	Pb*	Zn*
SAL 1	19 \pm 1.7	0.5 \pm 3.6	70 \pm 0.9	46 \pm 3.7	30.7 \pm 4.5	174 \pm 0.4	169 \pm 0.6
SAL 2	59 \pm 1.4	1.1 \pm 1.8	84 \pm 0.6	70 \pm 2.1	42.6 \pm 2.3	1381 \pm 1.5	332 \pm 1.0
SAL 3	905 \pm 3.6	36.8 \pm 0.2	81 \pm 5.9	501 \pm 0.4	94.6 \pm 0.4	29302 \pm 7.9	10620 \pm 5.6
SAL 4	140 \pm 0.8	2.2 \pm 1.8	75 \pm 0.8	61.8 \pm 1.9	30.5 \pm 1.9	1048 \pm 2.5	427 \pm 3.4
SAL 5	140 \pm 0.6	3.0 \pm 1.5	74 \pm 1.0	99 \pm 1.1	32.6 \pm 0.7	2452 \pm 1.9	540 \pm 1.9
SAL 6	1156 \pm 2.3	10.2 \pm 1.5	84 \pm 4.7	598 \pm 2.9	156.8 \pm 0.8	29286 \pm 5.3	5464 \pm 2.5
SAL 7	178 \pm 3.2	2.7 \pm 1.4	107 \pm 7.2	214 \pm 4	52.5 \pm 5.1	5071 \pm 1.9	959 \pm 4.1
SAL 8	266 \pm 0.9	3.7 \pm 1.2	74 \pm 1.0	147 \pm 1.3	39.8 \pm 1.2	4833 \pm 1.6	1522 \pm 4.3
SAL 9	398 \pm 0.9	9.0 \pm 1.8	93 \pm 6.9	238 \pm 4.7	38.2 \pm 2.9	7214 \pm 1.8	2172 \pm 3.9
SAL 10	178 \pm 0.9	2.8 \pm 1.1	93 \pm 6.9	127 \pm 1.7	31 \pm 4.5	2691 \pm 1.3	879 \pm 4.7
SAL 11	10 \pm 0.7	0.4 \pm 2.4	82 \pm 0.9	22 \pm 1.5	22.2 \pm 1.8	221 \pm 3.2	123 \pm 1.1
SAL 12	669 \pm 2.7	24.5 \pm 2.2	164 \pm 0.8	320 \pm 1.7	142 \pm 1.8	17443 \pm 6	3233 \pm 0.7
SAL 13	722 \pm 2.8	12.0 \pm 1.6	543 \pm 0.7	465 \pm 1.74	135 \pm 0.5	15024 \pm 10	4355 \pm 0.8
SAL 14	148 \pm 2.6	7.9 \pm 4.9	117 \pm 1.1	181 \pm 1.1	73 \pm 0.5	4266 \pm 12	2189 \pm 2.3
SAL 15	856 \pm 2.7	13.5 \pm 1.4	620 \pm 0.6	682 \pm 1.5	100 \pm 1.2	28709 \pm 28	7092 \pm 2.0
SAL 16	358 \pm 2.7	9.8 \pm 1.7	116 \pm 1.2	171 \pm 1.7	59 \pm 2.7	4968 \pm 16	1133 \pm 1.6
SAL 17	2816 \pm 4.6	23.6 \pm 1.0	121 \pm 0.3	404 \pm 1.3	96 \pm 1.3	22822 \pm 18	8488 \pm 4.2
SAL 18	61 \pm 2.6	1.8 \pm 9.9	402 \pm 1.1	102 \pm 1.4	55 \pm 1.6	1338 \pm 15	537 \pm 2.5
SAL 19	6502 \pm 2.9	43.7 \pm 0.9	93 \pm 0.9	104.7 \pm 0.7	56 \pm 1.3	33306 \pm 11	3268 \pm 1.2
SGVs/GAC	32 R , 43 A , 640 I	10 R , 1.8 A , 230 I	4.3 R , 2.1 A Cr(VI)	2330 R , 524 A	130 R , 230 A	450 RA , 750 I	3750 R , 618 A
			3000 A Cr (III)		1800 I		188000 I

*Concentrations measured using FAAS; R = Residential; A = Allotment; I = Industrial; Nos in italics represents the GAC values.

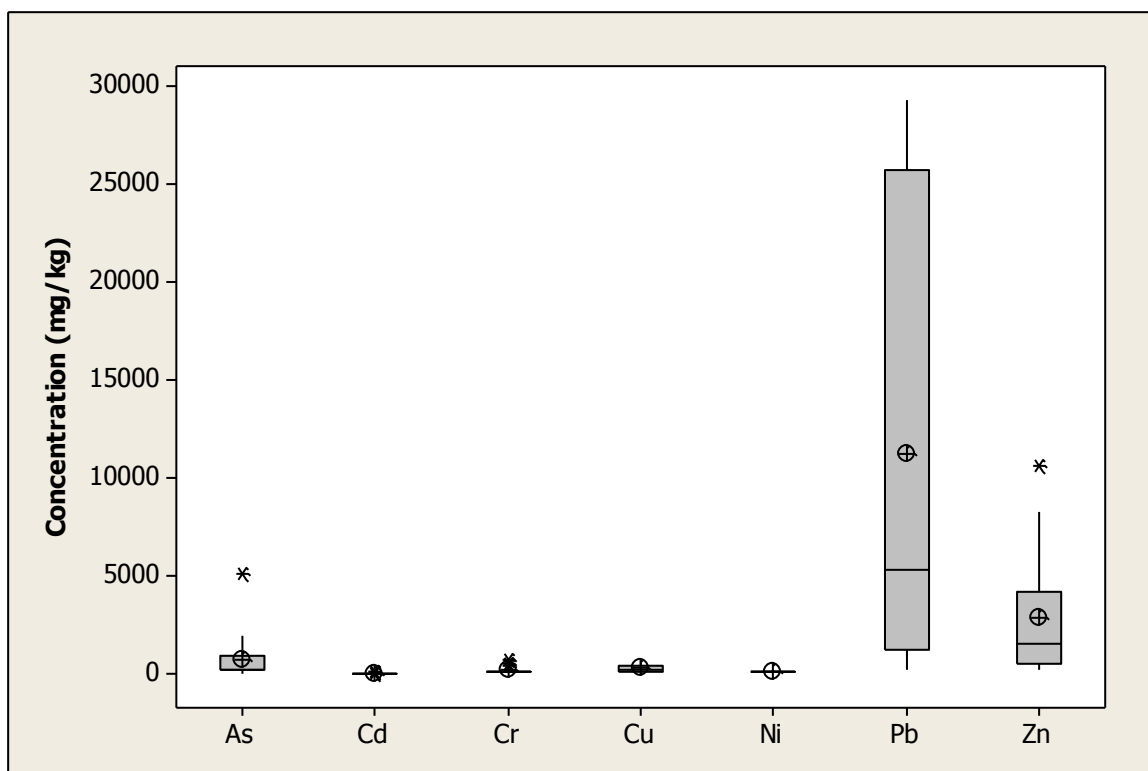


Figure 3.3: Boxplot of PTEs concentration in soil from former St Anthony's Lead works

3.3.4 Mobility of PTEs in soils from former St Anthony's lead works

Pseudo total PTE concentration is a useful guide in evaluating the pollution level in the environment. However, it does not give an estimate of how much of the PTE content that is bioavailable to a target organism. The single extraction using EDTA and HOAc has been used to demonstrate the fraction of the pseudo total content that is extracted from the soil by plant (plant available).

Table 3.9: Component matrix for data of St Anthony's Lead Works.

Elements	Components	
	1	2
As	0.285	0.541
Cd	0.367	0.475
Cr	0.187	-0.547
Cu	0.428	-0.315
Ni	0.383	-0.285
Pb	0.478	0.049
Zn	0.438	-0.014
Initial Eigenvalue	4.297	1.544
Percentage of variance	61.4	22.1
Cumulative percent	61.4	83.4

Correlation analysis has been carried out between the pseudo total PTE content and the single extraction using EDTA/HOAc and the results shown in Appendix D (A-G).

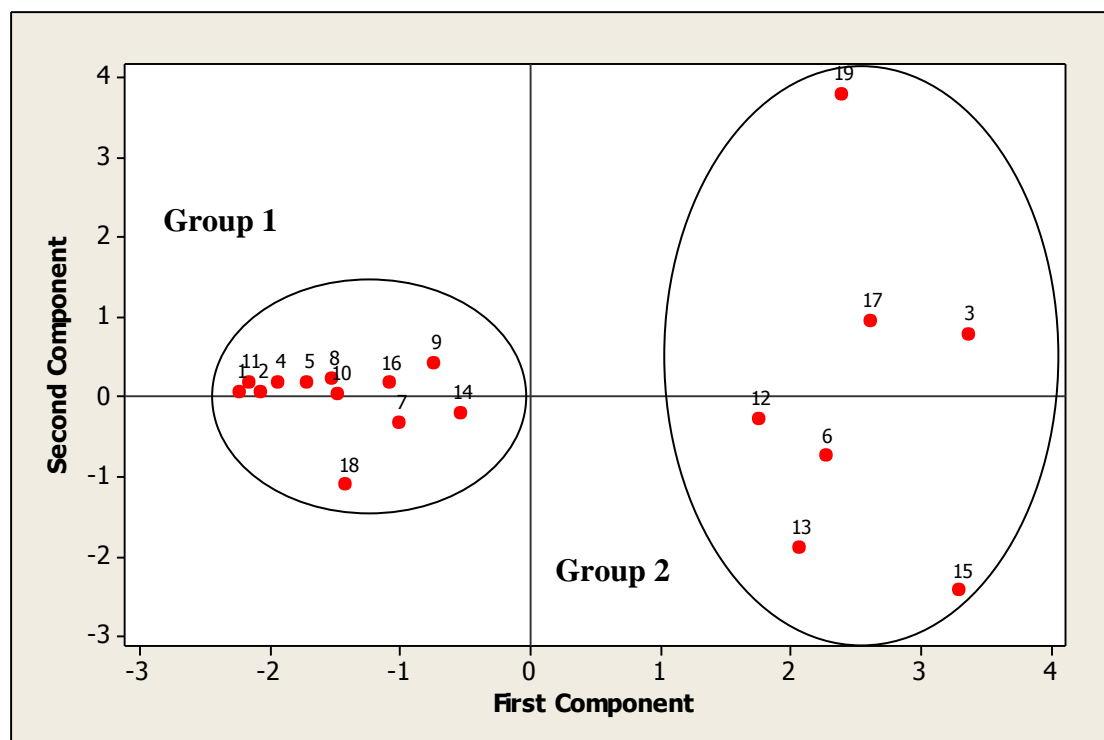


Figure 3.4: Biplot of the first two principal components. Each soil sample is numbered 1-19.

From the result, significant strong positive correlation between the EDTA/HOAc and the pseudo total concentration for all the PTEs measured were obtained. The correlation coefficients between EDTA and HOAc are as follows: - As (0.911), Cd (0.985), Cr (0.844), Cu (0.905), Ni (0.589), Pb (0.891) and Zn (0.816). Details of the extraction using EDTA and HOAc for individual elements are discussed below.

Arsenic (As)

The total concentration of Arsenic (As) in all the sample points is greater than the SGV for residential and allotment except for SAL 1 and SAL 11 whose concentration values are 21 and 15.2 mg/kg respectively. The SGV for residential is 32 mg/kg allotment is 43 mg/kg and commercial is 640 mg/kg. The concentration values for SALs 3, 6, 13, 15, 17 and 19 are well above the SGV for commercial. The percentage of As extracted (Figure 3.5) using EDTA is typically greater than those of HOAc in all the sample points except for SAL 3 and 6. The concentration of As extracted using EDTA ranges from 1.6 to 1235 mg/kg while that of HOAc ranges from 0.2 to 998.4 mg/kg. The higher extraction of As using EDTA is possibly

the result of its complexing ability (13). Site 6 has the highest value of mobility in all the sites for both HOAc and EDTA. This might be associated with the low value of CEC for

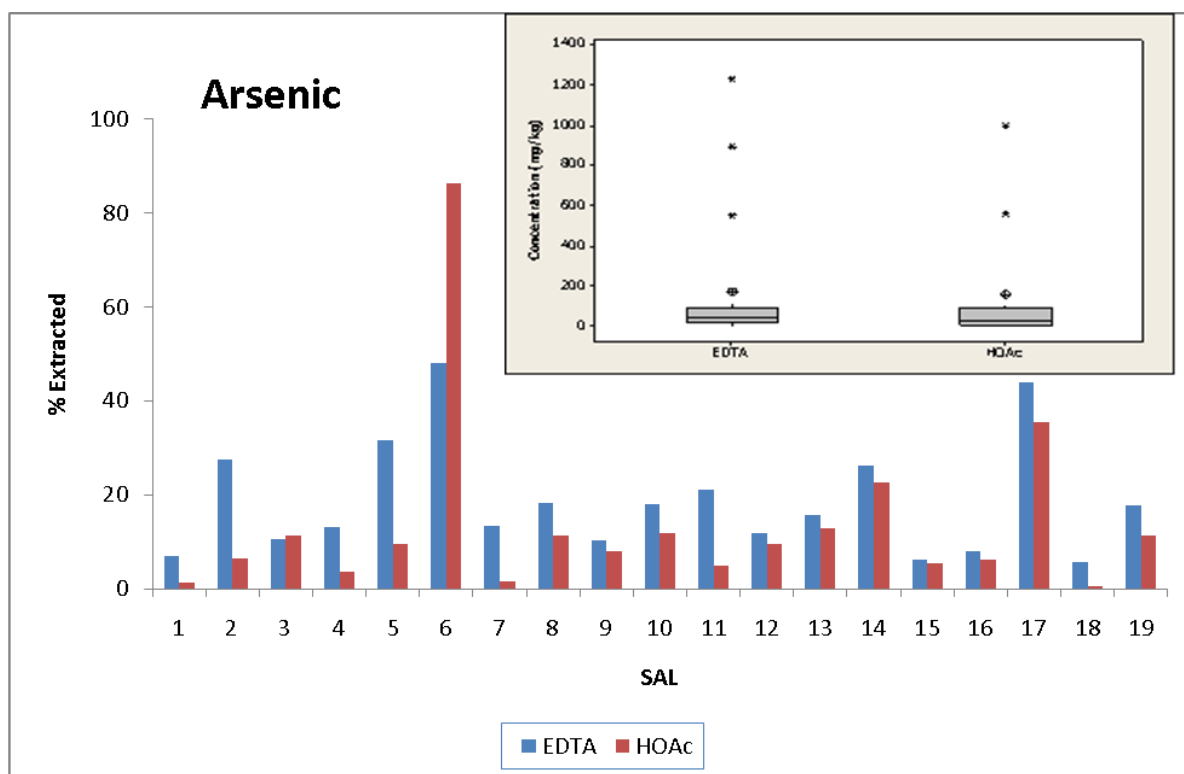


Figure 3.5: Percentage /concentration (mg/kg) of As extracted in EDTA and HOAc.

this sample point (Table 3.5) thereby leading to increased mobility. Similarly the lowest mobility is obtained in site 18 which can be as a result of a high pH (pH 8.10 Table 3.4) which contributes to the formation of precipitates, by increasing the number of adsorption sites and decreasing the competition of H^+ for adsorption, thereby increasing the PTE stability with humic substance. Also with a high value of CEC there is higher binding force and hence low mobility.

Cadmium (Cd)

As expected, the concentration of Cd in all the sample points is low compared to other metals measured. Though the concentrations are small, there is reasonable mobility of the metal in the sampled points except in SAL1 and 2 (Figure 3.6). The % of Cd extracted using EDTA is higher than those using HOAc. Cadmium is relatively mobile in surface water and ground water systems and exists mainly as hydrated ions or as complexes with humic acids and organic ligands such as EDTA (33). Sorption is influenced by the CEC of clays, carbonate minerals and organic matter present in the soil (34). SAL 18 has the highest CEC value and this implies low mobility of Cd as opposed to SAL 6 with high mobility. The % Cd extracted

using HOAc ranges from 6.4 to 53.9 (0.14 to 16.4 mg/kg) as opposed to that of EDTA which is 10.0 to 74.5 (0.07 to 14.9 mg/kg). The % extraction using HOAc is higher in SAL 3, 5, 7,

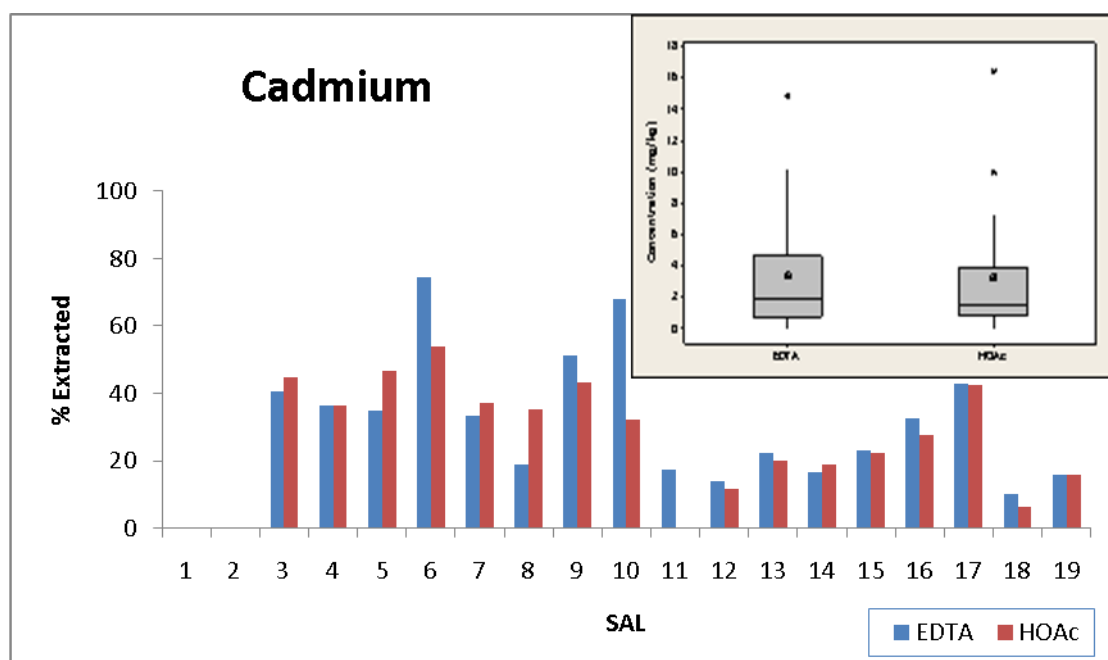


Figure 3.6: Percentage/concentration (mg/kg) of Cd extracted in EDTA and HOAc.

8 and 14 and an equal value of extraction using both EDTA and HOAc in SAL 19 and SAL 4.

Chromium (Cr)

All of the sampled points in this study had total soil Cr concentrations below the industrial/commercial SGV of 5000 mg/kg, although SAL 12, 13, 15 and 18 (with 173, 576, 655 and 404 mg/kg Cr respectively) exceed the SGV for residential and allotments (130 mg/kg). Using HOAc extraction, the mobility of Cr ranges from 0.2 to 21.7% total Cr (0.1 to 18.2 mg/kg) (Figure 3.7). Similarly using EDTA, the concentration extracted ranges from 0.1 to 2.7% of the total Cr (0.12 to 2.3 mg/kg). Of all the points sampled, Cr has the least mobility compared to other metals with the highest mobility obtained using HOAc except SAL 2 and 9 which has 0.4% extraction using the acid and 0.3% using EDTA.

Copper (Cu)

As earlier stated the concentration of Cu likely to exist in uncontaminated soil ranges from 5-20 mg/kg (Table 3.7). When these values were compared with the pseudo-total Cu concentration obtained in this work, all the sampled points showed elevated concentration.

The % of Cu extracted using EDTA ranges from 13.2 to 52.6 of the total Cu while that of HOAc ranges from 4.5 to 54.5 of the total Cu (Figure 3.8).

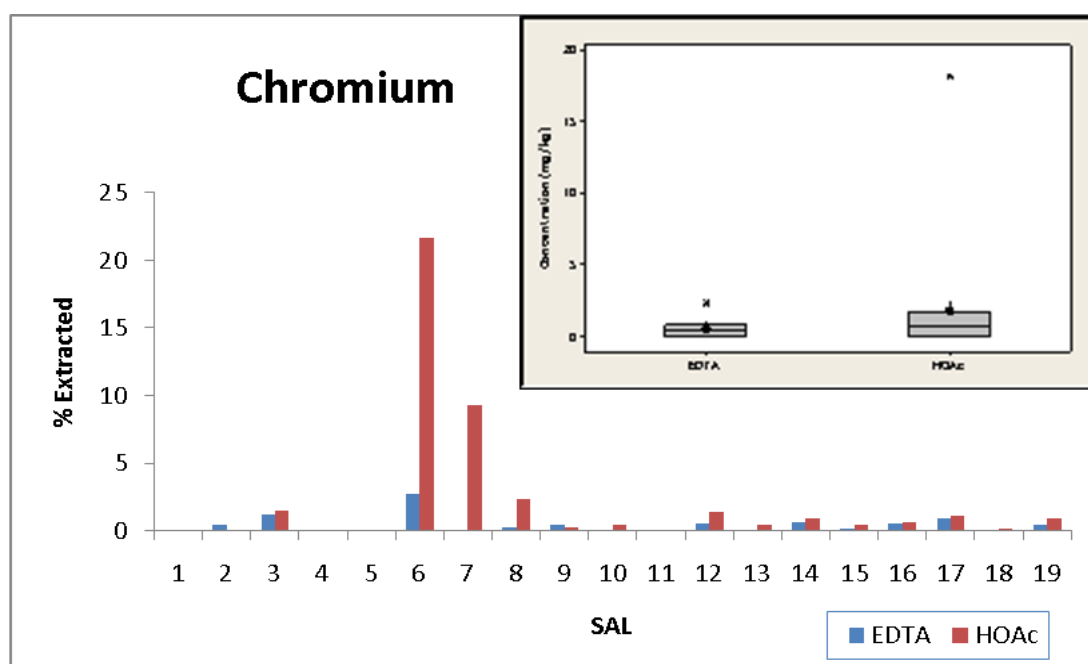


Figure 3.7: Percentage/concentration (mg/kg) of Cr extracted in EDTA and HOAc

The mobility of Cu determined by EDTA ranges from 8.4 to 315 mg/kg while that of HOAc ranges from 0.7 to 326 mg/kg and EDTA mobility is higher than that of HOAc except in SAL 6 and SAL 19. The HOAc extractable contents were approximately a factor of two to twelve times lower than that of EDTA except for SAL 8, 12, 13 and 15 which were less than twice those of EDTA. The lower values of HOAc extraction may be associated with the fact that HOAc only poorly breaks down strong copper-humic acid complex, as reported by *Whalley and Grant 1994 (35)*. Also the acetate anion is a less effective complexing ligand compared to EDTA which makes re-adsorption processes more likely (36). The effect of pH on copper mobility has been studied by many scholars (37-39). In all their studies they found out that the mobility of Cu increases with a decrease in pH. This is in agreement with the result obtained in Walker Riverside Park as shown in SAL 6 and 18 (Table 3.4). SAL 6 with the lowest pH (6.53) has the highest mobility in both HOAc and EDTA while SAL 18 with the highest pH has the least mobility.

Nickel (Ni)

All of the soils analysed have Ni concentration below that of the SGV for residential (130 mg/kg), except SAL 6 and 13 whose values are 140.4 and 136 mg/kg respectively. The SGV

for allotment and commercial are 230 and 1,800 mg/kg. These values are well above the concentrations of Ni in all the sampled points. The ability of Ni to form soluble complexes

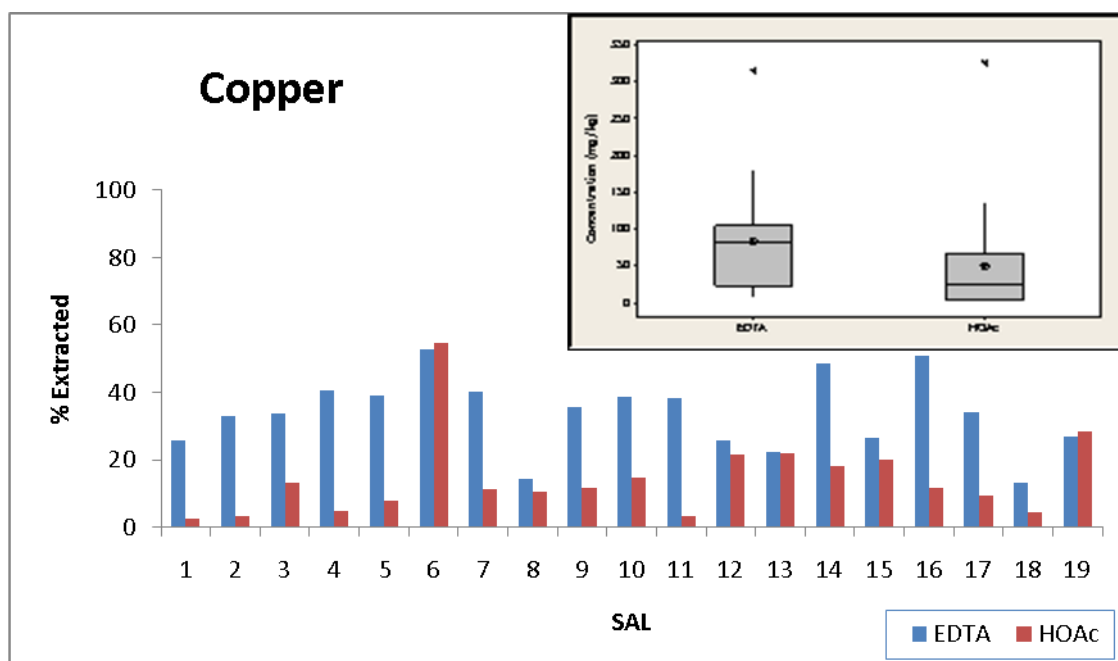


Figure 3.8: Percentage/concentration (mg/kg) of Cu extracted in EDTA and HOAc

with soil controls its mobility. In top soils, Ni binds to organic matter and can form soluble chelates which are more mobile in the presence of fulvic and humic acids (40). Soil pH is the most important factor controlling Ni solubility, sorption and mobility (41-43). The solubility and mobility of Ni increases with decreasing pH (42). From the results at the site, the lowest pH of 6.53 was found in SAL 6 (Table 3.4) and has the highest corresponding mobility in both EDTA and HOAc compared to other sampled points (Figure 3.9). SAL18 produces the highest pH (8.10) and has the lowest percentage mobility of 0.5 and 1.1 for HOAc and EDTA respectively. Of all the elements, Ni displays the least mobility in the soils at the site after Cr.

Lead (Pb)

Figure 3.10 show the % extracted using both extractants and the box plot of the concentrations. The concentrations of Pb from all the sampled points are well above the recently withdrawn SGV except SAL 1 and 11 whose values are 188 and 270 mg/kg respectively. The SGV for lead is 450 mg/kg for residential and allotment and 750 mg/kg for industrial (30). Lead has the highest overall concentration (Table 3.8) and the highest concentration in each of the sampled points. This is expected because this site was a former lead industrial site. Mobility of metals in soil depends among other things on the concentration of the metal in the soil. The mobility of Pb using EDTA ranges from 87 to

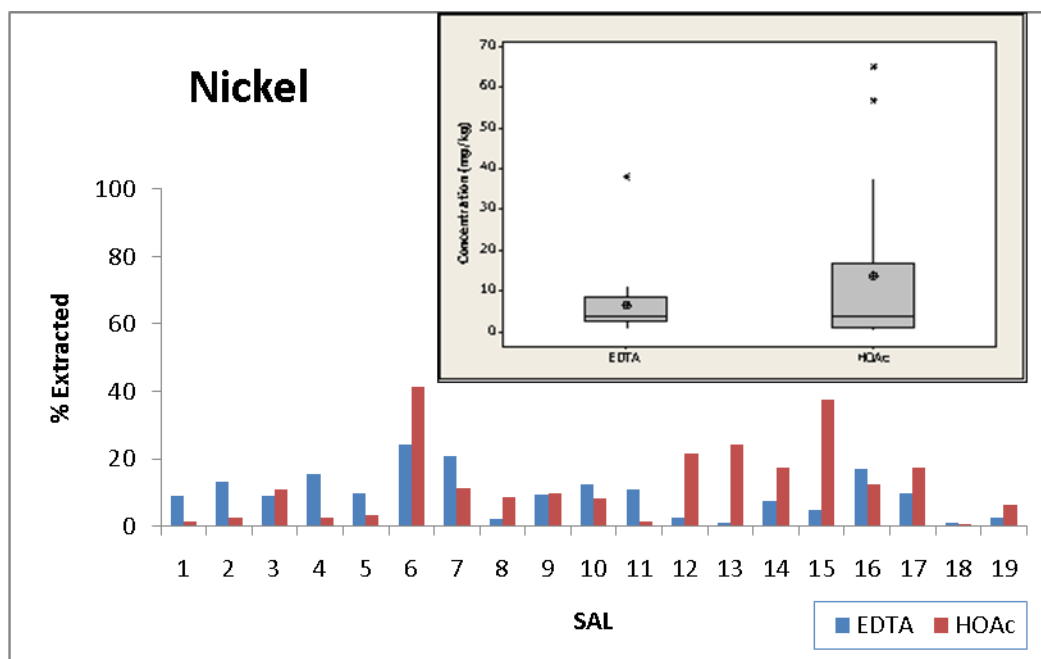


Figure 3.9: Percentage/concentration (mg/kg) of Ni extracted in EDTA and HOAc
 28,100 mg/kg and that of HOAc ranges from 12.5 to 17,100 mg/kg. The % of the total concentration of Pb extracted by EDTA and HOAc tends to mask the actual concentration extracted. For instance, the concentration of Pb extracted by EDTA in SAL 6 is 25,100 mg/kg and that for acetic acid is 16,100 mg/kg. These concentrations are extremely high, well above SGVs and the numbers reflect plant available rather than total concentration. From this result,

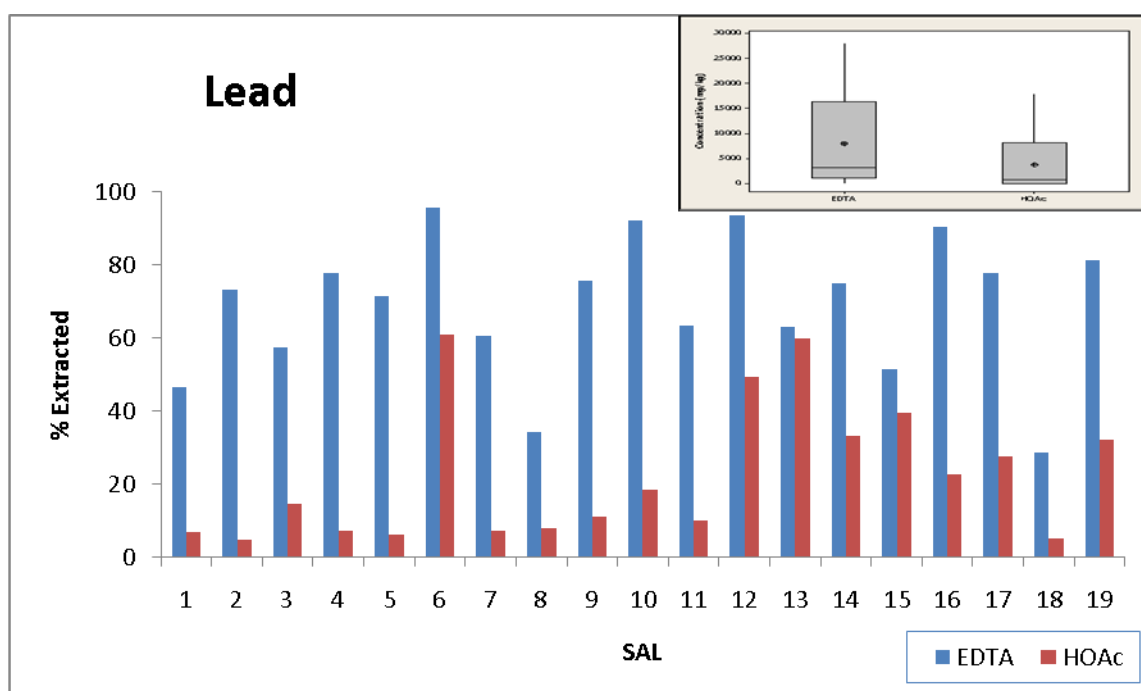


Figure 3.10: Percentage/concentration (mg/kg) of Pb extracted in EDTA and HOAc

additional risk assessment is required to consider the use of the site and extent of potential receptor exposure with respect to Pb.

Zinc (Zn)

All of the soils tested are well above the Zn GAC value for residential and plant uptake (320 mg/kg) except SAL 1 and 11 whose values are 169 and 144 mg/kg respectively. All of the soil tested is well below Zn GAC for commercial/industrial lands (188000 mg/kg). The mobility of Zn is higher in HOAc than in EDTA for the entire sample studied from the site (Figure 3.11)

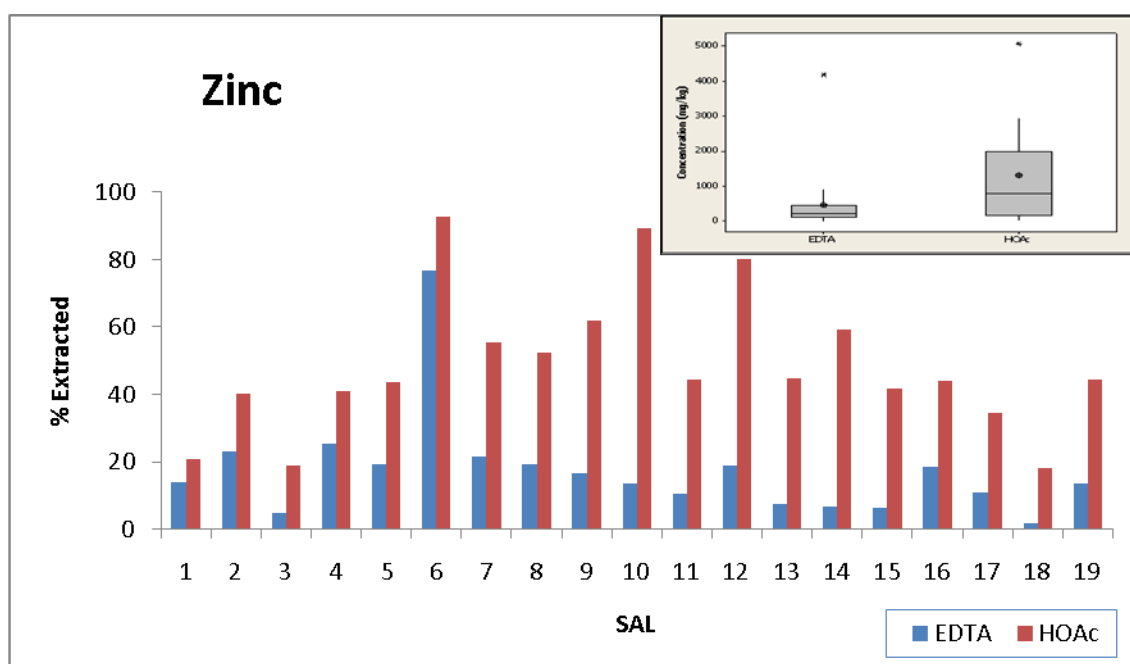


Figure 3.11: Percentage/concentration (mg/kg) of Zn extracted in EDTA and HOAc

Schafer *et al.*, 1998 (44) have classified several heavy metals according to their mobility properties. They observed that mobility of Zn is the highest and is the easiest to be transferred from one medium to another because it is present as soluble compounds at neutral and acidic pH values. Potentially mobile Zn concentration as measured in HOAc ranges from 54.4 to 5073 mg/kg with the highest corresponding to SAL 6, forming about 92.8% of the total concentration, while SAL 18 has the lowest percentage of about 18.2% of the total. The amount of Zn extraction using EDTA ranges from 10 to 4200 mg/kg.

3.3.5 Quality control for foraged fruit measurement

Samples of a plant certified reference material GBW 07603/NCS DC 73349 (bush branches and leaves) were analysed by ICP-MS in order to assess the accuracy and precision of this

approach following microwave digestion. Previous studies (45) have shown that elements with masses >80 amu can be analysed in standard mode whereas elements <80 amu should be analysed in CCT mode by ICP-MS. The results (Table 3.10) highlight the closeness of the data with the certified values and the good precision achievable. In addition, a comparison was also made with ED-XRF and the plant CRM. Good agreement with the certified values was obtained for all seven elements investigated using both ICP-MS and ED-XRF.

Table 3.10: Total PTE concentration (mg/kg, dry weight) in a plant certified reference material GBW 07603/ NCS DC 73349 (Bush branches and leaves).

Element	Isotope [^]	Bush branches and leaves GBW 07603 / NCS DC 73349			
		Certified value mean \pm SD	ICP-MS* measured value mean \pm SD		ED-XRF+ mean \pm SD
			Standard Mode	CCT Mode	
As	75	1.25 \pm 0.10	NA	1.21 \pm 0.17	1.27 \pm 0.82
Cd	111	(0.38)#	0.37 \pm 0.03	NA	0.60 \pm 0.03
Cr	52	2.6 \pm 0.1	NA	2.0 \pm 0.3	2.2 \pm 0.7
Cu	63	6.6 \pm 0.4	NA	6.4 \pm 0.4	6.2 \pm 0.6
Ni	60	1.7 \pm 0.2	NA	1.9 \pm 0.4	1.4 \pm 0.8
Pb	206	47 \pm 2	49 \pm 5	NA	43 \pm 7
Zn	66	55 \pm 2	NA	53.2 \pm 3.2	50 \pm 4

[^] for ICP-MS; * three sub-samples of each CRM was microwave digested and analysed by ICP-MS; + three sub-samples of the CRM was analysed by ED-XRF; # indicative value only; NA = not available.

3.3.6 Foraged fruits elemental concentration

In this study, the concentration of seven elements (As, Cd, Cr, Cu, Ni, Pb and Zn) in foraged fruits was determined by both ICP-MS and ED-XRF, for samples collected in September 2007 (Table 3.11), to assess the potential human health risk from their consumption. The use of comparable data from both ICP-MS and ED-XRF allows several scenarios to be investigated. For direct analysis of solid samples ED-XRF can be used to (a) rapidly acquire baseline data on major and minor elemental composition, and (b) provide a guide for the level of dilution required by ICP-MS prior to analysis. Good agreement was obtained between the two analytical techniques for the seven elements studied. The highest concentration of Cr was found in one of the sample of rosehips (7.3 mg/kg, dry weight) with the lowest levels in elderberry (1.2 mg/kg, dry weight). The highest concentration of Ni was found in one of the sample of rosehips (3.3 mg/kg, dry weight) with the lowest levels in another sample of rosehips (1.5 mg/kg, dry weight). In the case of Cu the highest concentrations were found in

Table 3.11: Analysis of foraged fruits from Site (SAL) (mg/kg, dry weight) mean \pm SD n=3 (September 2007)

Element	SAL 1		SAL 2		SAL 3		SAL 4		SAL 5		SAL 6	
	ICP-MS*	EDXRF+	ICP-MS*	EDXRF+	ICP-MS*	EDXRF+	ICP-MS*	EDXRF+	ICP-MS*	EDXRF+	ICP-MS*	EDXRF+
As	0.32 \pm 0.19	ND	0.32 \pm 0.05	ND	0.19 \pm 0.27	ND	ND	ND	0.23 \pm 0.10	ND	ND	ND
Cd	0.5 \pm 0.03	0.5 \pm 0.58	0.6 \pm 0.0 ₄	0.5 \pm 0.5	0.7 \pm 0.0 ₂	0.4 \pm 0.6	ND	ND	0.7 \pm 0.0 ₂	0.8 \pm 0.3	0.7 \pm 0.0 ₃	0.6 \pm 0.5
Cr	1.2 \pm 0.4	1.4 \pm 0.2	2.4 \pm 0.6	2.3 \pm 0.1	3.1 \pm 0.4	3.7 \pm 0.1	7.3 \pm 0.2	6.7 \pm 0.05	2.2 \pm 0.1	2.5 \pm 0.1	5.5 \pm 0.1	5.8 \pm 0.1
Cu	9.4 \pm 0.3	9.6 \pm 0.0 ₆	6.2 \pm 0.2	6.4 \pm 0.1	6.7 \pm 0.2	7.2 \pm 0.1	5.4 \pm 0.0 ₃	5.6 \pm 0.09	14.4 \pm 0.1	15.1 \pm 0.1	5.3 \pm 0.1	5.9 \pm 0.1
Ni	2.1 \pm 0.0 ₄	1.8 \pm 0.3	1.7 \pm 0.1	1.5 \pm 0.4	2.2 \pm 0.2	2.7 \pm 0.2	2.2 \pm 0.2	2.4 \pm 0.26	3.2 \pm 0.2	3.3 \pm 0.2	3.2 \pm 0.2	3.1 \pm 0.2
Pb	ND	ND	0.9 \pm 0.12	0.8 \pm 1.0	0.8 \pm 0.08	0.8 \pm 0.50	1.1 \pm 0.3	1.6 \pm 0.58	0.5 \pm 0.6	0.5 \pm 1.0	0.9 \pm 0.0 ₃	1.0 \pm 0.9
Zn	19.0 \pm 6.3	19.3 \pm 0.0 ₃	12.3 \pm 5.1	14.8 \pm 0.0 ₄	12.4 \pm 2.3	16.4 \pm 0.0 ₄	12.5 \pm 2.2	13.4 \pm 0.04	22.8 \pm 3.3	26.1 \pm 0.0 ₃	13.0 \pm 2.3	13.4 \pm 0.0 ₄

NOTE: SAL 1 = Elderberry, SAL 2 = Rosehips, SAL 3 = Rosehips, SAL 4 = Rosehips, SAL 5 = Black berry, SAL 6 = Sloes, * three sub-samples of foraged fruit were microwave digested and analysed by ICP-MS; + one sub-sample of foraged fruit was analysed three times by ED-XRF; **ND** = not detected

one of the sample of rosehips (15.1 mg/kg, dry weight) with the lowest levels in sloes (5.3 mg/kg, dry weight). Relatively high concentrations of Zn were found in all samples; typical levels were 26.1 mg/kg, dry weight in one of the sample of rosehips whilst another sample of rosehips had the lowest concentration (12.3 mg/kg, dry weight). The levels of the most toxic elements i.e. Cd and Pb were all below 1.6 mg/kg, dry weight (Rosehips) with the lowest levels in rosehips and elderberry (not detected). Samples were also obtained 12 months later to assess the potential influence of time on element concentration of foraged fruits from the same sampling locations (Table 3.13). In the samples of foraged fruits from September 2008 (Table 3.13) only microwave digestion followed by ICP-MS analysis was used. The box plot for the seasonal variation in concentration between 2007 and 2008 for the PTEs is shown in Figure 3.12. Unfortunately no sloes were obtained in September 2008. For samples obtained from the same sampling sites i.e. SAL 1-5 inclusive, the elemental concentration did not alter by a factor of 2 for any element with a concentration < 0.7 mg/kg, dry weight. Some notable exceptions to this were Cu in SAL 3 (rosehips) which altered in concentration from 6.7 ± 0.2 mg/kg, dry weight (September 2007) to 2.0 ± 0.3 mg/kg, dry weight (September 2008). Also SAL 4 (rosehips) which had significant element change for Cr from September 2007 to September 2008 and included 7.3 ± 0.2 mg/kg, dry weight to 1.3 ± 0.7 mg/kg, dry weight for Cr. It is difficult to directly compare the results from this study with the data reported in the literature because our concentrations are on a dry weight basis, whereas the literature concentrations are in fresh weight basis. Nevertheless, it has been possible to make an approximate comparison by converting our values to fresh weight using the experimentally determined moisture content as shown in Table 3.12.

Table 3.12: Comparison of own data with literature values for Blackberry from SAL 5

Elements	Experimentally determined data		Literature values
	Conc. (mg/kg) dry weight	Conc. (mg/kg) fresh weight+	Conc. (mg/kg) fresh weight (17)
As	0.23	0.003	N/A
Cd	0.70	0.010	0.0007-0.094
Cr	2.20	0.030	0.01-1.24
Cu	14.40	0.20	0.60-3.30
Ni	3.20	0.050	0.025-0.70
Pb	0.50	0.007	0.0128#
Zn	22.80	0.32	1.5-5.6

+ Based on calculated value using an experimentally determined moisture content of 70.5%.

Median value; N/A not available

Table 3.13: ICP-MS Analysis of foraged fruits from site (SAL)* (mg/kg, dry weight) mean \pm SD n =3 (September 2008)

Element	SAL 1	SAL 2	SAL 3	SAL 4	SAL 5	SAL 7	SAL 8
As	0.42 \pm 0.12	0.28 \pm 0.10	ND	ND	ND	0.37 \pm 0.03	ND
Cd	ND	ND	ND	ND	ND	ND	ND
Cr	1.7 \pm 0.6	1.6 \pm 0.5	2.4 \pm 0.4	1.3 \pm 0.7	2.6 \pm 0.4	1.2 \pm 0.7	1.3 \pm 0.5
Cu	6.4 \pm 0.3	6.3 \pm 0.3	2.0 \pm 0.3	6.4 \pm 0.3	11.6 \pm 0.2	6.5 \pm 0.3	6.5 \pm 0.2
Ni	2.3 \pm 0.3	3.2 \pm 0.4	1.9 \pm 0.3	1.1 \pm 0.3	2.5 \pm 0.2	0.9 \pm 0.4	1.6 \pm 0.3
Pb	1.91 \pm 0.4	0.17 \pm 0.1	0.23 \pm 0.4	0.16 \pm 0.8	0.32 \pm 0.2	0.16 \pm 0.4	0.15 \pm 0.7
Zn	24.6 \pm 4.2	16.1 \pm 3.9	23.4 \pm 3.6	14.6 \pm 3.8	22.0 \pm 3.4	17.8 \pm 3.9	16.2 \pm 3.2

NOTE: SAL 1 = Elderberry, SAL 2 = Rosehips, SAL 3 = Rosehips, SAL 4 = Rosehips, SAL 5 = Black berry, SAL 7 = Rosehip, SAL 8 = Rosehip, * three sub-samples of foraged fruit were microwave digested and analysed by ICP-MS. ND = not detected

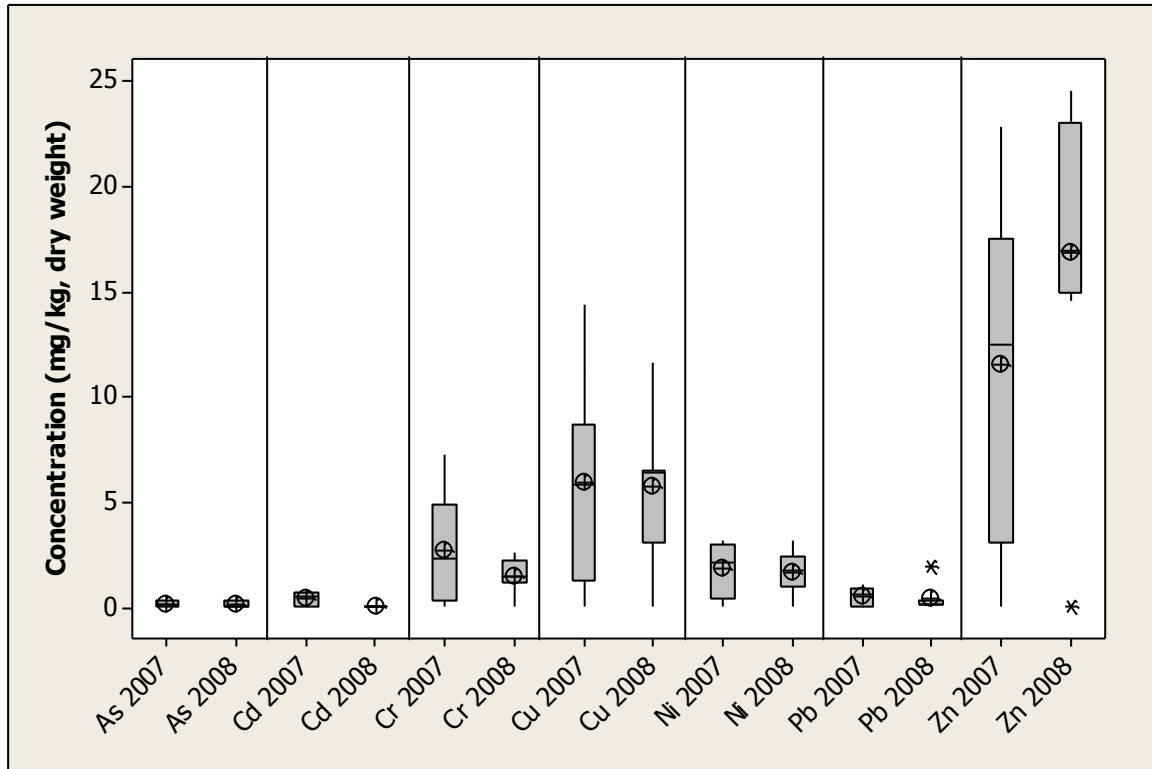


Figure 3.12: Boxplot showing seasonal variation in concentration for seven PTEs for 2007 and 2008

From Table 3.12, allowing for an approximation for moisture content, some of the element concentrations are within the ranges quoted, while some appears to be slightly lower in concentration (e.g. Cu, Ni, Pb and Zn) in the samples reported in this work. This finding goes to tell that though the site is heavily contaminated with PTE such as Pb, the amount taken by the foraged fruits is very small so may not likely pose any significant harm to the body when consumed.

3.3.7 Soil plant transfer factor

An approach to assess the uptake of elements in to plants from soil is to determine the transfer factor (TF). The transfer factor is defined (46-49) as shown in equation 3.6

$$TF = C_{\text{plant}} / C_{\text{pseudo total-soil}} \quad 3.6$$

where C_{plant} is the concentration of an element in the plant material (dry weight basis) and $C_{\text{pseudo total-soil}}$ is the total concentration of the same element in the soil (dry weight basis). In order to apply this approach two assumptions need to be made. The first is that the element contamination of soil in the specific sampling locations remains constant from one sampling season to another, and the second is that the foraged fruits and soils were sampled from approximately the same locations (within a distance of <2 m).

The PTE content of the site at the specified locations (Figure 3.2) was determined and is shown in Table 3.14. Elevated levels of Pb are noted throughout the site (the site is a former lead works); variations in the Pb content of the soil (range 188 to 28676 mg/kg) are location specific (Figure 3.2). Also high levels of Zn are noted (mean 2256 mg/kg with a range of 169 to 7023 mg/kg). The highest soil PTE levels are noted at sites SAL 5-8 with potential risk from toxic elements (i.e. As, Cd, Cr and Pb).

Table 3.14: Pseudo total content of PTEs in soil from the site (SAL)*(mg/kg, dry weight)

Metal	SAL 1	SAL 2	SAL 3	SAL 4	SA: 5	SAL 6/7	SAL 8
As	27 ± 4.7	61 ± 4.2	143 ± 4.8	204 ± 0.3	861 ± 2.7	604 ± 1.6	422 ± 0.3
Cd	0.5 ± 13.5	1.2 ± 3.4	5.1 ± 1.1	4.5 ± 0.9	12.5 ± 1.5	24.4 ± 2.7	11.7 ± 0.4
Cr	97 ± 5.2	100 ± 5.2	86 ± 6.8	66 ± 6.0	655 ± 1.0	173 ± 0.8	77 ± 6.2
Cu	36 ± 0.8	51 ± 0.6	94 ± 0.6	128 ± 0.5	715 ± 0.5	316 ± 1.1	197 ± 0.4
Ni	38.9 ± 0.9	40.4 ± 0.4	45.4 ± 0.5	42.2 ± 0.4	102 ± 0.9	149 ± 1.1	48.3 ± 0.4
Pb#	188 ± 0.7	1256 ± 1.9	2605 ± 1.8	3861 ± 1.8	28676 ±	19044 ±	7349 ± 1.3
Zn#	169 ± 0.9	387 ± 2.8	661 ± 2.0	1463 ± 2.4	7023 ± 0.7	3611 ± 2.0	2478 ± 1.9

* three sub-samples of soil were microwave digested and analysed by either ICP-MS or FAAS#

Using the PTE content of foraged fruits and soil from the same locations it was possible to assess the soil-to-plant transfer factors (Table 3.15) over two successive sampling seasons. It should be noted that no sloes were gathered in September 2008 due to their absence; consequently additional samples of rosehips were gathered from the same sampling site (SAL 7) and an additional site (SAL 8). Also the box plot for the transfer factor for the two seasons (2007 and 2008) is shown in Figure 3.13.

Transfer factors over successive seasons (for sites SAL 1-5) generally remained within a TF of ≤ 2 in terms of consistency. Exceptions were Ni in SAL 2 (multiplication factor of x 2.2); in SAL 3, Cu (multiplication factor 3.4) while in SAL 4 and Cr (multiplication factor 5.6). No trend was observable in these exceptions between elevated element levels in season 1 or 2. In all cases, except Cd in SAL 1 in 2007, the transfer factor was significantly <1.00 indicating that the majority of the element remained in the soil matrix and was not transferred in to the foraged fruit matrix.

Table 3.15: Transfer values for PTE uptake over two successive seasons.

Element	SAL 1		SAL 2		SAL 3		SAL 4		SAL 5		SAL 6		SAL 7		SAL 8	
	2007	2008	2007	2008	2007	2008	2007	2008	2007	2008	2007	2008	2007	2008	2007	2008
As	0.012	0.016	0.005	0.004	0.001	ND	ND	ND	0.000 ₃	ND	ND	NA	NA	0.000 ₆	NA	ND
Cd	1.000	ND	0.500	ND	0.137	ND	ND	ND	0.056	ND	0.029	NA	NA	ND	NA	ND
Cr	0.012	0.014	0.024	0.016	0.036	0.028	0.111	0.020	0.003	0.004	0.032	NA	NA	0.007	NA	0.017
Cu	0.261	0.180	0.121	0.124	0.071	0.021	0.042	0.050	0.020	0.016	0.017	NA	NA	0.020	NA	0.033
Ni	0.054	0.059	0.035	0.079	0.048	0.042	0.052	0.026	0.031	0.025	0.021	NA	NA	0.006	NA	0.033
Pb	ND	0.010	0.000 ₅	0.000 ₁	0.000 ₃	0.000 ₀	0.000 ₃	0.000 ₀	0.000 ₀	0.000 ₀	0.000 ₀	NA	NA	0.000 ₀	NA	0.000 ₀
Zn	0.112	0.146	0.032	0.042	0.019	0.035	0.009	0.010	0.003	0.003	0.004	NA	NA	0.005	NA	0.007

NOTE: SAL 1 = Elderberry, SAL 2 = Rosehips, SAL 3 = Rosehips, SAL 4 = Rosehips, SAL 5 = Black berry, SAL 6 = Sloes, SAL 7 = Rosehip, SAL 8 = Rosehip, ND = not detected; NA = no data as no foraged fruit sample taken.

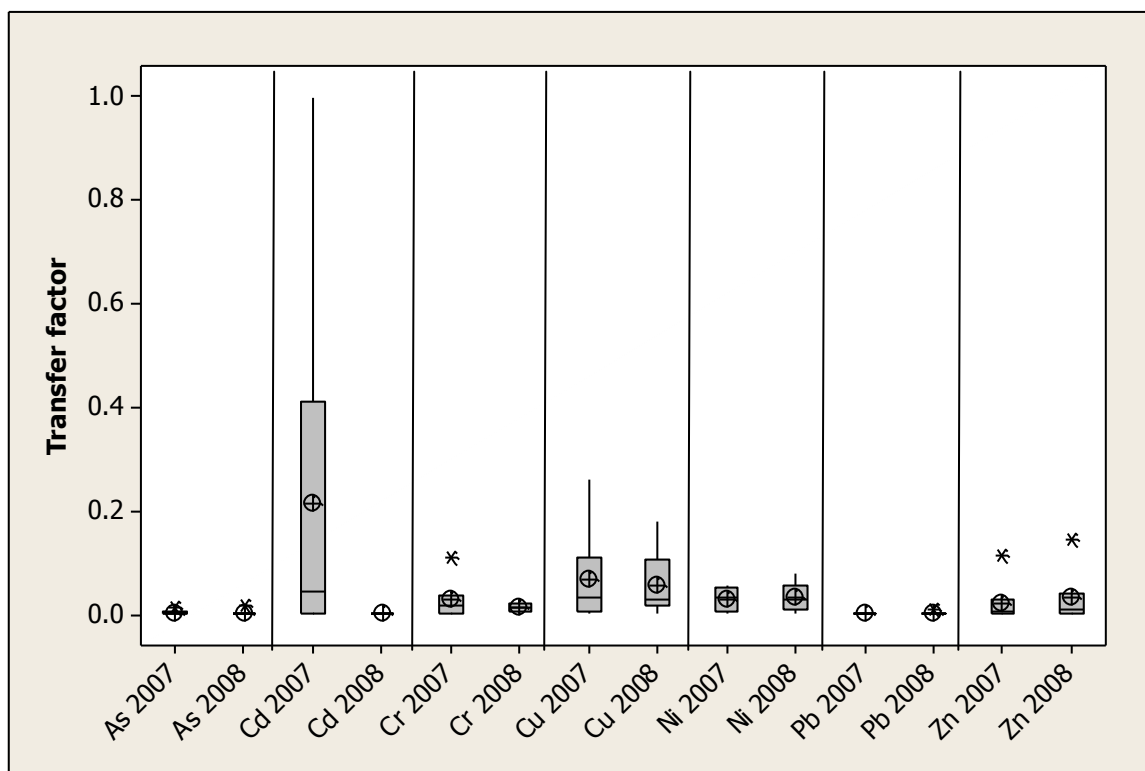


Figure 3.13: Box plot for transfer factors for the two seasons 2007 and 2008

3.4 Conclusion and implications for human health

The following conclusions can be drawn from this study

- (1) The site ranges from weakly acidic to neutral soil with low organic matter content while cation exchange capacity was within the normal range except SAL 18 (160.98 cmol/kg) which is above normal.
- (2) Elemental concentrations across the site are highly variable
- (3) Concentration plots and PCA analysis of the data from the site reveals that soil sample points SAL 3, 6.....SAL 19 have the highest PTE concentrations with Pb, As and Zn in excess of SGVs.
- (4) Table 3.8 shows that the concentration of most of the metals investigated exceed the SGVs/GAC. However, site specific circumstances such as the environmental pathways and site usage patterns of human receptors needs to be taken into account as exceedence does not necessarily imply that there is an actual risk to health. The particular chemical form and hence its extractability is also important. Chapter four details future work investigating the supplementary evidence to support risk assessment at such sites using oral bioaccessibility testing.

- (5) The plant availability estimated using EDTA/AcOH varies across the sampled points but correlates positively with pseudo total PTE concentration.
- (6) The elemental composition of foraged fruit over two sampling seasons shows that while the level of metal contamination in the soil is relatively high for some elements e.g. Pb, Zn and As the suspected risk to human health based on soil-to-plant transfer ratio is negligible.

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Chapter Four: The use of the physiologically-based extraction test to assess oral bioaccessibility of PTEs from an urban recreational site

4.1 Introduction

In the UK, the environmental health risk to humans of metals from contaminated land sites are currently assessed using the non-statutory Contaminated Land Exposure Assessment (CLEA) model (1). The model was developed to allow a comparison between predicted contamination exposure levels and known toxicological or Health Criteria Values (HCVs), to derive a Soil Guideline Value (SGV) which is both site and contaminant dependant (2). These SGVs are generic assessment criteria that assess the risks to human health from chronic exposure to contaminated soil. On that basis SGVs are classed as intervention values and any exceedance may indicate an unacceptable human health risk from that contaminated site (3). Derivation of SGVs using the CLEA model assumes that the contaminant is released from the soil and is taken up by the human body to the same extent as the model which has been used to determine the HCV (for that contaminant) (3); this assumption may, of course, not be true as the HCVs may have been determined using non-human material and more soluble form of the contaminant (4). Therefore basing the human health risk of contaminants from contaminated soils on SGVs assumes that all the contaminant is taken up by the systemic circulation; this over-simplification negates both the insolubility of the contaminant and its potential sequestration within the soil (5). Researchers are therefore investigating alternate approaches that allow a better representation of the likely oral bioaccessibility (i.e. extractable in the human gut) of contaminants (6). Any estimation of the oral bioavailability of soil-bound contaminants is based on the principle that uptake (i.e. absorption) of the contaminant depends on its release (i.e. bioaccessibility) in the gastro-intestinal (GI) track (7, 8). The approaches are often described using *in vitro* method. It is therefore important in assessing human health risk assessment to consider the oral bioaccessibility of the contaminant, determined using *in vitro* methodology, from contaminated land sites.

A range of *in vivo* approaches have been evaluated to assess the bioavailability of PTEs for humans from a variety of matrices including soil, dust and food (9-11), the information obtained using these approaches cannot always be related to humans due to differences in physiology, contaminant and the matrix itself (12). So while some work does continue on *in vivo* approaches considerable barriers exist not least relating to ethical governance issues as well as financial constraints, such that *in vitro* approaches are becoming more prevalent. The

in vitro approaches have been developed to simulate both the stomach and intestinal juices. A number of comparative studies have suggested that the bioaccessibility results obtained are largely dependent on the specific *in vitro* conditions used, the actual contaminant under investigation and the sample matrix (1, 7-8). As the new CLEA model software (13-14) allows greater functionality and the incorporation of bioaccessibility data into site specific risk assessments the development of robust and agreed protocols is appropriate and timely.

This work investigates the oral bioaccessibility of PTEs in soil from a former industrial site which is now an open access urban green space used for recreational purposes in Newcastle upon Tyne. While much of the literature reported data on bioaccessibility has focused on As and Pb, this study investigates a broad range of elements (As, Cd, Cr, Cu, Ni, Pb and Zn), all of which may be present in elevated concentrations due to the sites known industrial legacy. In addition, the magnitude and spatial variability across the site of the oral bioaccessible fraction is also of inherent interest.

4.2 Experimental

4.2.1 The study site

The study site, sample collection strategy and preparation along with soil characterisation as well as the apparatus needed for the experiment has already been described in 3.1.1, 3.2.1-3.2.5.

4.2.2 Reagents

In addition to the reagents used in 3.2.2, for the physiologically-based extraction test the following reagents were required. Sodium hydrogen phosphate (NaH_2PO_4) and potassium hydrogen phosphate (KH_2PO_4) were obtained from Baker Scientific, UK. Sodium chloride (NaCl), potassium thiocyanate (KSCN), anhydrous sodium sulphate (Na_2SO_4), potassium chloride (KCl), calcium chloride ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$), ammonium chloride (NH_4Cl), sodium bicarbonate (NaHCO_3), magnesium chloride ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), sodium hydroxide (NaOH), hydrochloric acid (HCl), 30% hydrogen peroxide, urea, uric acid, anhydrous D+ glucose, D-glucosaminehydrochloride, pepsin (pig), bovine serum albumin (BSA) and pancreatin (pig) and concentrated nitric acid (69%, HNO_3) were all obtained from Merck (Poole, England). Mucin (pig) was obtained from Carl Roth, Germany. D-glucuronic acid (Fluka) and

α -amylase (bacillus species), lipase (pig) and bile salts (bovine) were obtained from Sigma.

4.2.3 Preparation of extraction reagents for the *in vitro* extraction test

The *in vitro* extraction test is based on the BARGE method (15). Essentially simulated saliva fluid was prepared by first adding 145 mg of amylase, 50.0 mg mucin and 15.0 mg uric acid to a 2 L HDPE screw top bottle. Then, 896 mg of KCl, 888 mg NaH₂PO₄, 200 mg KSCN, 570 mg Na₂SO₄, 298 mg NaCl and 1.80 mL of 1.0 M HCl was added into a 500 mL volume container and made up to the mark with water (*inorganic saliva components*). In to a second 500 mL volume container was added 200 mg urea and made up to the mark with water (*organic saliva components*). Then, the 500 mL of inorganic and 500 mL of organic saliva components was simultaneously poured in to the 2 L HDPE screw top bottle. The entire content of the screw top bottle was shaken thoroughly and the pH of the solution (gastric simulated saliva fluid) measured and was found to be within the range 6.5 ± 0.5 .

Simulated gastric fluid was prepared by first adding 1000 mg of bovine serum albumin, 3000 mg mucin and 1000 mg pepsin to a 2 L HDPE screw top bottle. Then, 824 mg of KCl, 266 mg NaH₂PO₄, 400 mg CaCl₂, 306 mg NH₄Cl, 2752 mg NaCl and 8.30 mL of 37% HCl were added separately into a 500 mL volume container and made up to the mark with water (*inorganic gastric components*). In to a second 500 mL volume container was added 650 mg glucose, 20.0 mg glucuronic acid, 85.0 mg urea and 330 mg glucosamine hydrochloride and made up to the mark with water (*organic gastric components*). Then, the 500 mL of inorganic and 500 mL of organic components were poured simultaneously in to the 2 L HDPE screw top bottle. The entire content of the screw top bottle was shaken thoroughly and the pH of the solution (gastric simulated fluid) measured. The pH was found to be within the range 0.9-1.0. The combination of mixed saliva fluid (1 mL) and gastric fluid (1.5 mL) was checked and was in the range of pH 1.2 – 1.4.

Simulated duodenal fluid was prepared by first adding 200 mg of CaCl₂, 1000 mg bovine serum albumin, 3000 mg pancreatin and 500 mg lipase to a 2 L HDPE screw top bottle. Then, 564 mg of KCl, 80 mg KH₂PO₄, 50.0 mg MgCl₂, 5607 mg NaHCO₃, 7012 mg NaCl and 180 μ L of 37% HCl was separately added into a 500 mL volume container and made up to the mark with water (*inorganic duodenal components*). In to a second 500 mL volume container was added 100 mg urea and made up to the mark with water (*organic duodenal components*). Then, 500 mL of inorganic and 500 mL of organic duodenal components was simultaneously poured in to the 2 L HDPE screw top bottle. The entire content of the screw

top bottle was thoroughly shaken and the pH of the solution (simulated duodenal fluid) was measured. The pH was found to be within the range 7.4 ± 0.2 .

Simulated bile fluid was prepared by first adding 222 mg of CaCl_2 , 1800 mg bovine serum albumin and 6000 mg bile to a 2 L HDPE screw top bottle. Then, 376 mg of KCl, 5785 mg NaHCO_3 , 5259 mg NaCl and 180 μL of 37% HCl was separately added in to a 500 mL volume container and made up to the mark with water (*inorganic bile components*). In to a second 500 mL volume container was added 250 mg urea and made up to the mark with water (*organic bile components*). Then, 500 mL of inorganic and 500 mL of organic bile components was simultaneously poured in to the 2 L HDPE screw top bottle. The entire content of the screw top bottle was shaken thoroughly and the solution allowed to stand for approximately 1 hour, at room temperature, to allow for complete dissolution of solid reagents. The pH of this solution (simulated bile fluid) was measured and was found to be within the range 8.0 ± 0.2 . The pH for the combined saliva fluid (1.0 mL), gastric fluid (1.5 mL), 3.0 mL duodenal fluid and 1.0 mL bile fluid was checked to be within the range 6.3 ± 0.5 .

4.2.4 Preparation of samples using BARGE method

‘Gastric’ Extraction. An accurately weighed sample (0.6 g) was placed into a 50 mL screw-cap Sarstedt tube and treated with 9 mL of simulated saliva fluid by manually shaking the soil-fluid mixture in the screw-cap vessel. Then, after 5 – 15 mins 13.5 mL of simulated gastric fluid was added. This was followed by shaking the mixture on an end-over-end shaker maintained at $37 \pm 2^\circ\text{C}$ for 1 h. At that stage the pH of each soil suspension was checked (the pH should be maintained between 1.2 -1.7). The solution was then centrifuged at 3000 rpm for 5 min and a 1.0 mL aliquot of supernatant removed. Finally, 9.0 mL of 0.1 M HNO_3 was added to the supernatant and the extract stored at $< 8^\circ\text{C}$ prior to analysis by ICP-MS.

‘Gastric + Intestine’ Extraction. An accurately weighed sample (0.6 g) was placed into a 50 mL screw- cap Sarstedt tube and treated with 9 mL of simulated saliva fluid by manually shaking the soil-fluid mixture in the screw-cap vessel. Then, after 5 – 15 mins 13.5 mL of simulated gastric fluid was added. The mixture was then shaken on an end-over-end shaker maintained at $37 \pm 2^\circ\text{C}$ for 1 hour. Then, the pH of the soil suspensions was checked such that the pH was maintained between 1.2 -1.7. Following this 27.0 mL of simulated duodenal fluid and 9.0 mL of simulated bile fluid were added by manually shaking the soil-fluid

mixture in the screw-cap vessel. The pH of the resultant suspension was adjusted to 6.3 ± 0.5 , by the dropwise addition of 37% HCl, 1 M or 10 M NaOH, as required. The mixture was again shaken on an end-over-end shaker maintained at $37 \pm 2^\circ\text{C}$ for 4 h. Then, the soil suspension was removed and its pH measured (and record); the pH should be maintained between 6.3 ± 0.5 . The soil suspension was then centrifuged at 3000 rpm for 5 min and a 1.0 mL aliquot of supernatant removed. Finally, 9.0 mL of 0.1 M HNO_3 was added to the supernatant and it was stored at $< 8^\circ\text{C}$ prior to analysis by ICP-MS.

4.2.5 Microwave digestion protocol/ICP-MS analysis of sample

See sections 2.4.3 and 3.2.6 for details

4.2.6 Determination of oral bioaccessibility

The oral bioaccessibility of PTEs from soil can be determined using the BARGE procedure. The percentage bioaccessible fraction (% BAF) can be calculated using equation 4.1

$$\text{Bioaccessible fraction (\%)} = \frac{C_{\text{Bioaccessibility}}}{C_{\text{pseudo total}}} \times 100 \quad 4.1$$

Where, $C_{\text{Bioaccessibility}}$ = Concentration of PTE released from soil (mg/kg) obtained via BARGE stage I (gastric) or stage II (gastric + intestinal); $C_{\text{pseudo total}}$ = Pseudo total concentration of PTE in soil (mg/kg).

4.3 Results and Discussion

4.3.1 Evaluation of the BARGE approach: Application to soil CRM

At the moment, there is no CRM for bioaccessibility testing as a result, the assessment to the accuracy of the BARGE was derived using a mass balance type approach adopted and applied to a soil certified reference material (GBW 07401). Initially, using the microwave digestion approach, the CRM was analysed for 7 PTEs under investigation and the results compared to the certified values. The results (Table 4.1) show good accuracy (and precision, based on triplicate determinations) between the measured and certified values for all PTEs studied. Then, the BARGE protocol was followed on the same CRM and data obtained on the PTE content (using ICP-MS) for both the gastric digest (stage I) and gastric + intestinal digest (stage II). Finally, the residual fraction from stage II was acid digested using the microwave protocol described above and also analysed by ICP-MS. In terms of the mass balance it is noted that the sum of stage II and the residual fraction digest are in close agreement with both the certified CRM values and the pseudo-total PTE content, determined

using the microwave digestion protocol, with recoveries between 80.4 and 123.3% (compared to certified values) and 81.6 and 110.4% (compared to pseudo-total values). The sum of stage II and the residual fraction show increased imprecision in data as might be expected, based on cumulative errors. It is noted that the largest percentage bioaccessibility fraction (% BAF) is obtained for stage II digests for all PTEs considered, however, the % BAF varies according to the PTE ranging from 6.8% for Cr to 83.3 for Cd.

4.3.2 Characterization of study site topsoils

Each of the soils collected in this study was characterised for pH, loss on ignition (as indicative of soil organic matter content) and cation exchange capacity. The results, shown in Table 4.2, indicate that the pH of the soils from the study site were largely neutral (pH range 6.5 – 8.1, with a median pH value of 7.4) while the loss on ignition data indicated soil organic contents ranging from 6.4 to 24.7 %, with a median value of 10.7 %. Finally, the cation exchange capacity (CEC) of the soil ranged from 9.4 to 161.0 cmolc/kg with a median value of 21.4 cmolc/kg. Also in Table 4.2 is a summary of the PTE concentration across the site for the 7 elements studied.

4.3.3 Evaluation of the BARGE approach: Application to an urban recreational site

The summary data of bioaccessibility for the 19 topsoils are presented (Table 4.3). Reporting bioaccessibility data as % BAF conceals the actual concentration of the element in the extract and is also highly dependent on the determined total concentration, which itself may be liable to the vagaries of the extraction technique (i.e. total v pseudo-total). As such the minimum, median and maximum metal concentration determined for each extraction stage are presented and the % BAF is only presented for the worst-case scenario sample (i.e. for the maximum determined PTE concentration at each extraction stage; Table 4.3). For completeness the amount of PTE that remained in the soil after gastric + intestinal digest is also shown i.e. the concentration of PTE that remained in the residual digest. As might be expected, the % BAF varies across the range of PTEs as well as the individual sample locations. The extraction stage (i.e. the gastric or the gastric and intestinal stage) which exhibited the highest concentration, and hence highest % BAF was consistently the gastric and intestinal stage (see Appendix A). Of the 19 topsoils, all the PTEs investigated predominantly indicated higher extracted PTE content following the gastric and intestinal stage compared to gastric stage only.

Table 4.1: Analysis of soil certified reference material (GBW 07401) using microwave digestion and the BARGE method.

Element	Certified value Mean ± SD (mg/kg) (n = 3)	Pseudo-total metal Mean ± SD (mg/kg) (n = 3)	BARGE <i>in vitro</i> Extraction Test				Residual fraction digest		Total metal (stage II + residual fraction) Mean ± SD (mg/kg) (n = 3)	% Recovery based on pseudototal metal concentration
			Stage I (gastric digest)		Stage II (gastric and intestinal digest)		Mean ± SD (mg/kg) (n = 3)	%Residual*		
			Mean ± SD (mg/kg) (n = 3)	% BAF+	Mean ± SD (mg/kg) (n = 3)	%BAF+				
As	34 ± 5	34.8 ± 5.4	11.2 ± 3.6	32.2	16.1 ± 2.9	46.3	20.8 ± 6.3	59.8	36.9 ± 12.8	106
Cd	4.3 ± 0.6	4.8 ± 1.2	2.2 ± 1.3	45.8	4.0 ± 1.1	83.3	1.3 ± 3.2	27.1	5.3 ± 5.6	110.4
Cr	62 ± 6	61.5 ± 0.5	2.3 ± 4.6	3.7	4.2 ± 5.2	6.8	48.6 ± 5.1	79.0	52.8 ± 14.9	85.9
Cu	21 ± 2	20.0 ± 2.3	5.2 ± 1.4	26.0	11.4 ± 1.1	57.0	7.8 ± 3.2	39.0	19.2 ± 5.7	96
Ni	20.4 ± 2.7	20.1 ± 2.9	3.6 ± 3.5	17.9	5.1 ± 3.9	25.4	11.3 ± 3.2	56.2	16.4 ± 10.6	81.6
Pb	98 ± 8	99.3 ± 0.1	14.3 ± 1.3	14.4	18.2 ± 9.2	18.3	78.1 ± 4.02	78.7	96.3 ± 14.5	96.9
Zn	680 ± 39	660.9 ± 3.0	180 ± 24	27.2	258 ± 37	39.1	418 ± 33	63.2	676 ± 94	102

+ % **BAF**: stage related bioaccessibility, calculated as a fraction of the pseudo-total; * % **Residual**: residual fraction calculated as a fraction of the pseudo-total.

Table 4.2: Topsoil properties (n = 19). PTE concentration (mg/kg, dry weight)

Soil parameter	Minimum	Maximum	Mean	Median	Standard deviation
pH	6.5	8.1	7.3	7.4	0.5
LOI (%)	6.4	24.7	11.5	10.7	4.1
CEC (cmol _c / kg)	9.4	161	28.6	21.4	34.4
As	15.0	5062	683	204	1161
Cd	0.5	45.9	11.8	7.1	12.7
Cr	66.0	655	168	100	165.7
Cu	24.0	715	238	180	196.7
Ni	37.3	149	72.2	55	36.6
Pb	188	29302	11215	5256	11269
Zn	144	10620	2887	1463	2995

Note: LOI = loss on ignition; CEC = cation exchange capacity

Table 4.3: Summary of stage related bioaccessibility and residual fraction of PTEs in all topsoils.

Element	BARGE <i>in vitro</i> extraction test (mg/kg) (n = 19)						Residual digest (mg/kg) (n = 19)		
	Stage 1 (Gastric digest)			Stage 2 (Gastric + Intestinal digest)			minimum	median	maximum
	Minimum	Median	maximum (% BAF+)	minimum	median	maximum (% BAF+)			
As	3.4 ± 0.9	92 ± 3.5	2134 ± 6.3 (32.8%)	6.0 ± 1.1	160.0 ± 3.0	3366 ± 3.4 (51.8%)	5.6 ± 2.3	103 ± 2.1	3167 ± 25 (62.6%)
Cd	0.3 ± 2.5	4.1 ± 2.5	19.03 ± 0.3 (51.7%)	0.30 ± 0.5	4.70 ± 2.0	29.3 ± 6.3 (67.1%)	0.2 ± 7.1	2.5 ± 2.2	15.3 ± 6.3 (33.3%)
Cr	17.1 ± 3.4	22.9 ± 3.3	208 ± 2.9 (33.5%)	29.0 ± 6.6	42.5 ± 7.0	400 ± 21 (64.5%)	31.5 ± 2.9	54.7 ± 2.9	323 ± 3.9 (62.6%)
Cu	6.2 ± 3.2	25.4 ± 2.0	131.4 ± 2.0 (26.2%)	15.9 ± 4.1	109.4 ± 3.5	472 ± 1.9 (69.2%)	8.9 ± 2.8	55.9 ± 2.1	201.1 ± 7.9 (35.9%)
Ni	4.1 ± 1.1	15.6 ± 2.2	44.9 ± 1.4 (31.6%)	7.30 ± 8.3	26.70 ± 3.7	75.10 ± 7.8 (47.9%)	13.4 ± 2.5	30.3 ± 2.4	84.4 ± 5.1 (60.1%)
Pb	65.5 ± 5.0	1811 ± 5.0	13653 ± 4.7 (40.9%)	94.0 ± 3.0	2331 ± 5.2	15374 ± 4.5 (46.2%)	92.2 ± 4.0	2540 ± 5.3	19940 ± 44 (69.5%)
Zn	31.1 ± 6.6	616 ± 5.1	3806 ± 6.2 (35.8%)	53.0 ± 7.7	881 ± 3.9	6013 ± 2.1 (56.6%)	70.8 ± 5.4	645 ± 3.3	4802 ± 2.9 (58.5%)

+ % **BAF**: bioaccessibility data for the sample exhibiting the highest concentration, calculated as a fraction of that samples pseudo-total for stage I or Stage II; * % **Residual**: residual fraction calculated as a fraction of the pseudo-total for the soil exhibiting the highest residual concentration.

A boxplot of all the data is shown in Figure 4.1. It is noted that the highest bioaccessible fraction is observed for Cd with Cu exhibiting the second highest values.

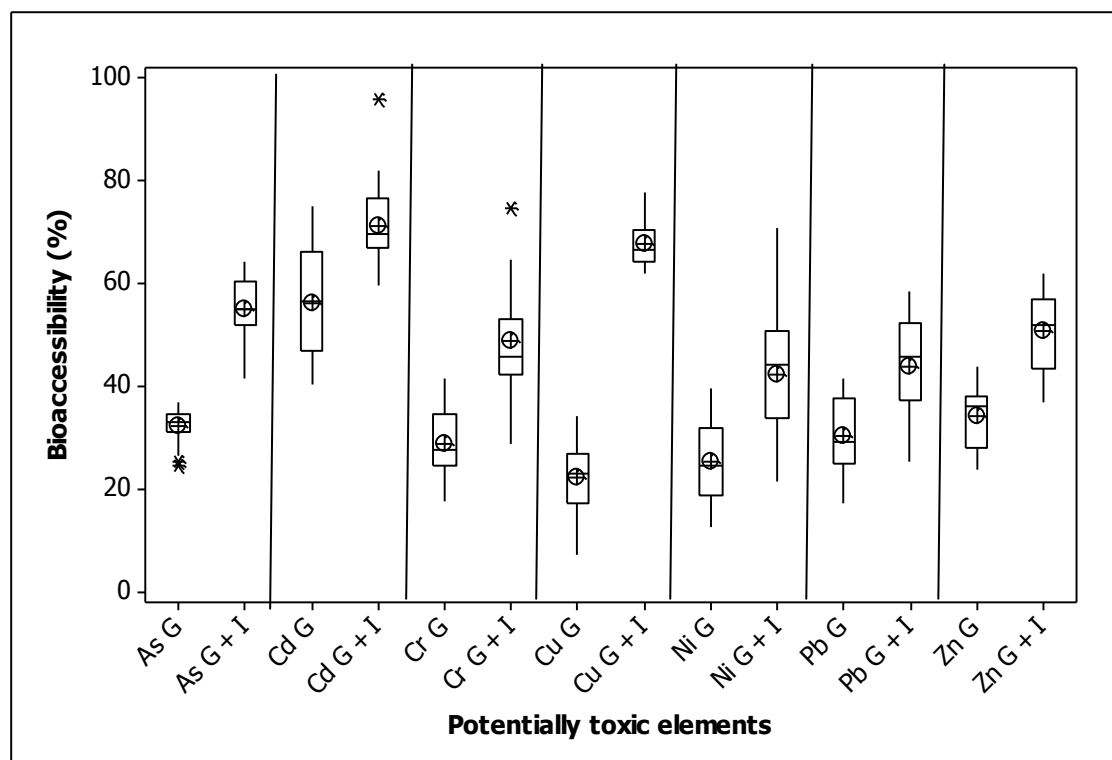


Figure 4.1: Box plot for bioaccessibility of As, Cd, Cr, Cu, Ni, Pb and Zn in topsoils

The bioaccessibility data shows variation across the site both spatially and between different PTEs but largely mirrors the pseudo-total concentrations. The relationship between the % LOI and the % BAF was computed graphically and is shown in Appendix E. From the graph, there is no clear relationship between %LOI and %BAF in this site. It has been reported that the relationship between total concentration and the bioaccessible fraction is not necessarily linear (16), however in this case a high correlation exists. The correlation coefficients were calculated using the pseudo-total PTE concentrations and the bioaccessible PTE concentrations (i.e. BAF from the gastric + intestinal stage); the values are As (r^2 0.9978), Cd (r^2 0.9597), Cr (r^2 0.9144), Cu (r^2 0.9630), Ni (r^2 0.7990), Pb (r^2 0.8959) and Zn (r^2 0.9554).

In terms of the overall bioaccessibility, the % BAF (computed based on gastric + intestinal) ranges are as follows: As (42-64%), Cd (60 – 96), Cr (29 – 74), Cu (62 – 78), Ni (21 – 71), Pb (25 – 58) and Zn (37 – 62). These values are less than the 100% assumed in CLEA model indicating that some of the PTEs are retained in the soil matrix of the residue.

Most researchers observed high bioaccessibility of some metals in the stomach phase example: Roussel et al., 2009 (17) observed that Cd, Pb and Zn are more bioaccessible in the stomach with %BAF of 68, 62 and 47 respectively, Lamb et al., 2009 (18) in their study discovered that Pb is more bioaccessible in the stomach with %BAF of over 80 while the rest (Cu, Zn and Cd) was more in the intestinal phase, Turner et al., 2007 (19) observed more Cd and Zn in the stomach phase, Poggio et al., 2009 (20) observed higher bioaccessibility of Pb and Zn in the stomach while Cu and Ni were in the intestinal phase. In the present research, high bioaccessibility is observed in the intestinal phase (G+I) than in the stomach phase for all the metals studied. This is not surprising considering the fact that absorption normally occurs in the intestine and bioaccessibility actually measures the fraction which is absorbed in the blood stream during digestion.

4.3.4 Generic risk assessment and the role of bioaccessibility data

As noted in section 1.4, the UK uses the widely accepted source–pathway–receptor paradigm of pollutant linkage to assess human health risks from contaminated land (21-22). On that basis the key exposure pathways that are considered appropriate for this site have been identified as follows: (i) direct ingestion of soil (while the site is largely vegetated it does have exposed soil particularly on the steep-sloped shrubby/wooded areas); (ii) direct ingestion/inhalation of dust (dust generation, via digging at the site) the potential for accumulation of soil material on footwear and its subsequent transport into buildings where it may be inhaled is limited, however, dust is more likely risk); and (iii) ingestion of soil attached to ‘vegetables’ (the seasonal foraging of wild fruits and berries does occur). These aspects will be considered based on the measured data.

It is possible to compare the BAF results from this work with the published SGVs. However, following a review of SGVs (3) only a limited number of values are available for use in generic risk assessment. Of relevance to this work SGVs are available for As, Cd and Ni (23-25). However, generic assessment criteria (GAC) values have been published for Cr, Cu and Zn (16) and so have been used to compare the data against. The lack of an updated SGV for Pb means that the data in this work for Pb have been compared with the previous value (that was withdrawn in July 2008) (1). On that basis a generic quantitative risk assessment for this site was able to be carried out. It should also be noted that an urban recreational space is not considered as part of the land scenarios inherent within the SGV/GAC values. On that basis the data on this work was compared to SGV/GAC values for both allotment and residential

land use scenarios. [Note: Exceedance of SGV/GAC values of the total elemental concentration in soil is indicative of a potential risk to human health for users of the site. However, in this case (an urban recreational site) the assumptions on which the SGV/GAC values are determined (i.e. age, sex and frequency of use) may not be the most appropriate].

A comparison of the determined pseudo-total element concentrations with the SGV/GAC guidelines provides the following observations. In the case of As, 17 out of 19 samples exceed the lower SGV (residential scenario) of 32 mg/kg; also 17 samples exceed the higher SGV (allotment scenario) of 43 mg/kg with 5 soil samples exceeding the SGV (allotment scenario) by almost 20 times. For Cd, 16 out of 19 soil samples exceed the lower SGV (allotment scenario) of 1.8 mg/kg, and 7 out of 19 samples exceed the higher (residential scenario) SGV of 10 mg/kg. For Cr, if the concentration represents Cr (VI) then all soil samples exceed the residential scenario of 4.3 mg/kg, as well as the allotment scenario of 2.1 mg/kg with all samples having more than 15 times the GAC values in both scenarios. If however, the concentration represents Cr (III) then none of the soils exceed even the lowest GAC value of 3,000 mg/kg (allotment scenario). For Cu, 2 out of 19 soil samples exceed the lower GAC (allotment scenario) of 524 mg/kg; none of the soil samples exceed the higher GAC (residential) of 2,330 mg/kg. For Ni, 3 out of 19 samples exceed the lower SGV (residential scenario) of 130 mg/kg; however, none of the 19 samples exceeds the higher SGV (allotment scenario) of 230 mg/kg. For Pb, 17 out of 19 soil samples exceed the allotment & residential scenario of 450 mg/kg, with concentrations in 17 soils at more than twice the SGV and a maximum soil concentration of 33,306 mg Pb/kg. While finally for Zn, 13 out of 19 soil samples exceed the lower GAC value (allotment scenario) of 618 mg/kg; 5 soil samples also exceed the higher (residential scenario) of 3,750 mg/kg, with concentrations more than twice the GAC value (i.e. maximum soil concentration of 10,620 mg Zn/kg).

Therefore based on the generic risk assessment criteria, a high percentage of soil samples, for all of the 7 elements investigated, indicate further investigation may be required.

Unfortunately, as already indicated, differences between this site conceptual model and the inherent assumptions within the generic land use scenarios mean that the estimated exposure could well be different. The use of oral bioaccessibility data may therefore contribute to a better understanding of the generic risk assessment. Also, as previously highlighted, the SGVs (except Pb) all assume that the contaminants are completely available to the receptor

following exposure; as this is unlikely it will lead to an overestimate of the exposure from the soil.

Consideration of the bioaccessible data, based on the concentration of element in the gastric + intestinal stage (rather than the value for %BAF), allows a modified view to emerge for some elements. In terms of Cr, and specifically Cr (VI) and Cr (III), no changes occur as a result of using the bioaccessible data i.e. all data exceeds the GAC values for residential and allotment scenarios. In summary, in the case of As, 15 samples still exceed residential and allotment scenarios (a change of two fewer); for Cd, 1 sample fewer exceeds the allotment scenario and 3 fewer the residential scenario; for Cu and Ni, no samples exceed the allotment or residential scenarios; for Pb, 16 still exceed the allotment & residential scenario; while for Zn, 3 fewer exceed the allotment scenario and 4 fewer exceed the residential scenario. It is concluded that while only a small shift in emphasis is made by the use of bioaccessibility data the approach does have merit. This is because the assumptions made about the use of SGV/GAC values and the land scenarios (allotment and residential) may not adequately reflect the urban recreational site chosen to study in this work. In addition, it should be borne in mind that the generic SGVs are based on the following soil type: a sandy loam soil with 6 % soil organic matter content (26). The current site soil property data identifies typically higher organic matter content, based on the loss on ignition values being indicative of soil organic matter (Table 4.2). This, coupled with the high cation exchange capacity values, is likely to make the soils more naturally retentive of the elements under investigation than those in the generic models (22).

4.3.5 Estimation of bioaccessibility of soil using TDI and MDI

The potential health risk of soil ingestion can be assessed by calculating the mass of sample that a child would require to ingest to reach the estimated tolerable daily intake (TDI) or mean daily intake (MDI) for each of the potentially toxic elements investigated. The values of the TDI are shown in Table 4.4 and are based on a 10 kg child, while the values for the MDI are based on a child aged between 5-6 years of age and which corresponds to a weight of 20 kg (27). In the case of As, a non-threshold carcinogen, a TDI is inappropriate. An oral index dose (ID_{oral}) has been proposed of $0.3 \mu\text{g kg}^{-1} \text{bw day}^{-1}$ for As (28). Therefore based on the ID_{oral} value and an assumed body weight of a 10 kg child the ingestion value is assumed to be 3 $\mu\text{g/day}$. The US EPA (29) has recommended values for daily soil (including soil and outdoor settled dust), indoor settled dust and soil plus dust ingestion for children.

Table 4.4. Amount (µg) of PTE ingested from the sampled SAL soil calculated from the content of PTEs(mg/kg) and assumptions of daily soil ingestion rates of 50 g (soil-geophagy), 1 g (soil-pica) and 0.1 g (guideline value based on unintentional consumption)(29). Particle size <250 µm, Tolerable daily intake (TDI) values and mean daily intake (MDI) for a child weighing 10 kg for TDI and 20kg for MDI are also presented.

Element	50 g/day ingestion rate	1 g/day ingestion rate	0.1 g/day ingestion rate	Bioaccessible concentration+ (0.1g / day)	TDI ^a µg/day	MDI µg/day
As	13300	266	26.6	33.7	3*	5 ^b
Cd	395	7.9	0.8	0.3	5	28.7 ^e 13.4 ^c
Cr (III)	4650	93	9.3	4.0	50,000	60.2 ^e
Cu	8550	171	17.1	4.7	1400	7000 ^e
Ni	2750	55	5.5	0.8	500	130 ^d
Pb	248400	4968	496.8	153.7	36	N/A
Zn	76100	1522	152.2	60.1	5000	27000 ^e

+ based on the maximum bioaccessible concentration using either the ‘gastric’ or ‘gastric + intestinal’ phase; in accordance with the TDI (ID_{oral}) the calculation is based on a child weighing 10 kg.

* oral index dose (ID_{oral}) value of 0.3 µg kg⁻¹ bw day⁻¹ (28) and assuming a child weighing of 10 kg.

^a reference (30); ^{b-d} references (28, 31-32); ^e reference (16); N/A = not available.

The recommended guideline value for soil and dust ingestion has been assessed to be 100 mg/day for children between the age 1 and <6 years. In addition, for children up to age 14 who may exhibit soil-pica behaviour the estimates range from 400 to 41,000 mg/day with a recommended upper percentile soil pica ingestion rate of 1,000 mg/day (pica was defined in the report (29) as the recurrent ingestion of unusually high amounts of soil); while the recommended upper percentile geophagy soil estimate is 50,000 mg/day (geophagy was defined in the report (29) as the intentional ingestion of earths, usually associated with cultural practices). Therefore on the basis of these recommendations, the amount of PTE ingested from the soil sample was calculated based on 50 g/day (geophagy), 1 g/day (soil-pica) and 0.1 g/day (guideline value based on unintentional ingestion). The values obtained were compared with the TDI (or ID_{oral} in the case of As) and MDI values to assess the risk of the PTE to the child. From the results for a child with geophagy behaviour the levels of all PTEs are exceeded except Cr (III). In contrast for a child with pica behaviour (1 g/day) only two PTE exceeds the TDI value i.e. Cd and Pb; in addition, for As, the ID_{oral} value and the MDI values are exceeded. Based on the unintentional consumption of 0.1 g of soil, only Pb and As exceed the guideline value (TDI and ID_{oral} respectively) for this type of samples. Though these calculations can help to estimate the potential risk from the urban environment studied they only assume ingestion (oral) as the means of exposure. Inhalation and subsequent transfer to the gastro-intestinal tract via coughing up and re-swallowing may also be relevant to consider.

4.4 Conclusion

Our generic quantitative risk assessment highlighted that exceedances of the SGV (for either residential or allotment landuse) were present for all of the 7 PTEs based on pseudo-total concentrations. Site-specific circumstances, such as critical pathways, receptors, site-usage patterns and activities, need to be taken into account and so exceedence does not necessarily imply that there is an actual risk to health.

One objective of this work was to apply a robust *in vitro* GI procedure to soils sampled across a former industrial site in NE England, and to highlight the role of such data for use in human health risk assessment. The results indicated that the bioaccessibility of PTEs investigated in soils across the site is less than the 100% assumed by the CLEA model. Cadmium however, indicated a much higher %BAF than other analytes with over 50 % of the pseudo-total Cd concentration bioaccessible in all the 19 soils investigated. The bioaccessibility data indicated

both elemental and spatial differences and highlight total soil concentration to be a rather crude estimate of the fraction that is potentially extractable in the body and hence potentially taken into the blood stream. Given too that the generic land use categories (allotments and residential) are a very conservative screening tool for an area of public open space a detailed qualitative risk assessment is recommended as part of the on-going risk assessment at this site, along with a detailed user study to identify exposure duration of the various receptor groups. Site-specific SGVs/GAC need to be refined on the basis of soil type, the PTE bioaccessibility data, and receptors behaviours, as this might lower or increase their exposures. Bioaccessibility data are an additional tool towards a more holistic multidisciplinary approach to understanding human health risk at contaminated site.

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Chapter Five: Natural and anthropogenic PTE input to urban street dust and the role of oral bioaccessibility testing

5.1 Introduction

Dust is solid matter which comprises soil, anthropogenic metallic constituents and natural biogenic materials (1). The soil component of urban street dusts is a mixture of mineral constituents and organic matter; the anthropogenic materials are vehicle exhaust particles, lubricating oil residues and tyre, brake and engine wear components while the natural biogenic materials are tree leaves and other plant matter pulverized by traffic and general weathering (2-4). Some of the most common elements associated with automobile industries include As, Cd, Cu, Ni, Pb and Zn, either within the fabrication of a vehicle, component parts (e.g. brake pads), as additives (e.g. in lubricants) for engine operation or resulting from automobile corrosion (5, 6). For example, Cu compounds are used in lubricants as anti-wear agents, by providing a protective layer on engine surfaces to reduce friction and prevent damages due to continuous rubbing between engine parts. Historically, lead compounds (lead tetraethyl ($C_2H_5)_4Pb$) were added as antiknock agents in petrol prior to their cessation in the UK in 1999 (7). The now wide spread use of unleaded fuels however, has not put a stop to the use of lead compounds in motoring activities; for example, lead compounds are used as anti-wear agents in lubricant oils for engines (5). Among the alternatives added into lubricant oils are Zn compounds (5). For example, zinc dialkyldithiophosphate (ZDDP) is added as an agent to provide additional protection under extreme-pressure or in a heavy-duty performance situation to protect the lubricant itself from oxidative breakdown and to prevent the formation of deposits in engines (5, 8, 9). Metals such as Ni are also used for plating the outer part of a vehicle, such as, the tyre rims or as an alloy for plating the surface of the cylinder and pistons of an engine (10). The source of Ni in road dust is believed to result from corrosion of these components over the lifetime of the vehicle (11-13).

Road dust can be a particular risk to humans due to its small particle size and its inherent mobility in windy weather conditions leading to the possibility of direct and indirect exposure; direct exposure from dust can occur by inhalation while indirect exposure results from contact with exposed skin and outer clothing which in turn can be accidentally ingested (14). Young children (up to 5 years of age) are more likely to ingest significant quantities of dust than adults because of the behaviour of mouthing non-food objects and repetitive hand / finger sucking during outdoor activities (15). Also children have a much higher absorption

rate of PTEs from the digestion system and higher haemoglobin sensitivity to heavy metals than adults (16). While many studies of total metal content in street dust have been carried out (13, 17-27) little has been published on the potential sources (natural or anthropogenic) of the street dust (28, 29) and the environmental health risk to humans from the unintentional ingestion of this material. Initial work has focused on the determination of the total metal content of street dust and its likely anthropogenic or natural origin. The oral bioaccessibility of metals in urban road dust has received relatively little attention compared with other environmental solids i.e. soils. Therefore, in this chapter it is the indirect exposure route that is considered using an oral bioaccessibility approach. However, inhalation sources are likely also to be an important source particularly since traffic related particulates are a very fine fraction. The bioaccessible fraction is the total amount of the metal in dust which could be released during digestion. This released fraction represents the maximum amount of contaminant available for intestinal absorption that may exert toxicity (30). It can be assessed using an *in vitro* physiologically-based extraction test (PBET). The urban site chosen for the study is the city of Newcastle upon Tyne, north east England. Sampling took place within the city centre from pedestrianised sites around the main shopping areas and close to the city centre road network.

5.2 Experimental

5.2.1 Sampling and Sample preparation

Road dusts / sediments (> 10 g) were collected from nine different sites (Figure 5.1) using hand brushing with a plastic brush and plastic collection pan. This was achieved by sweeping with the brush and pan (31, 32). Each brush and pan was considered disposable and used only once. A number of identical dustpan and brushes were used in the present study and the sampling process was kept consistent in order to minimize sampling variability. A description of the sample sites is shown in Table 5.1. The samples collected were put in a sample bag and dried in the oven at 40°C for several days. Then, the samples were passed through a plastic sieve of mesh size 250 µm to separate into <250 and > 250µm particle size fractions.

5.2.2 Instrument and reagents

See 3.2.2 and 4.2.2

5.2.3 Pseudo total PTE concentration

See 2.4.3 and 3.2.6

5.2.4 Procedure for *in vitro* physiologically based extraction test

See 4.2.3 and 4.2.4 as described elsewhere (33).

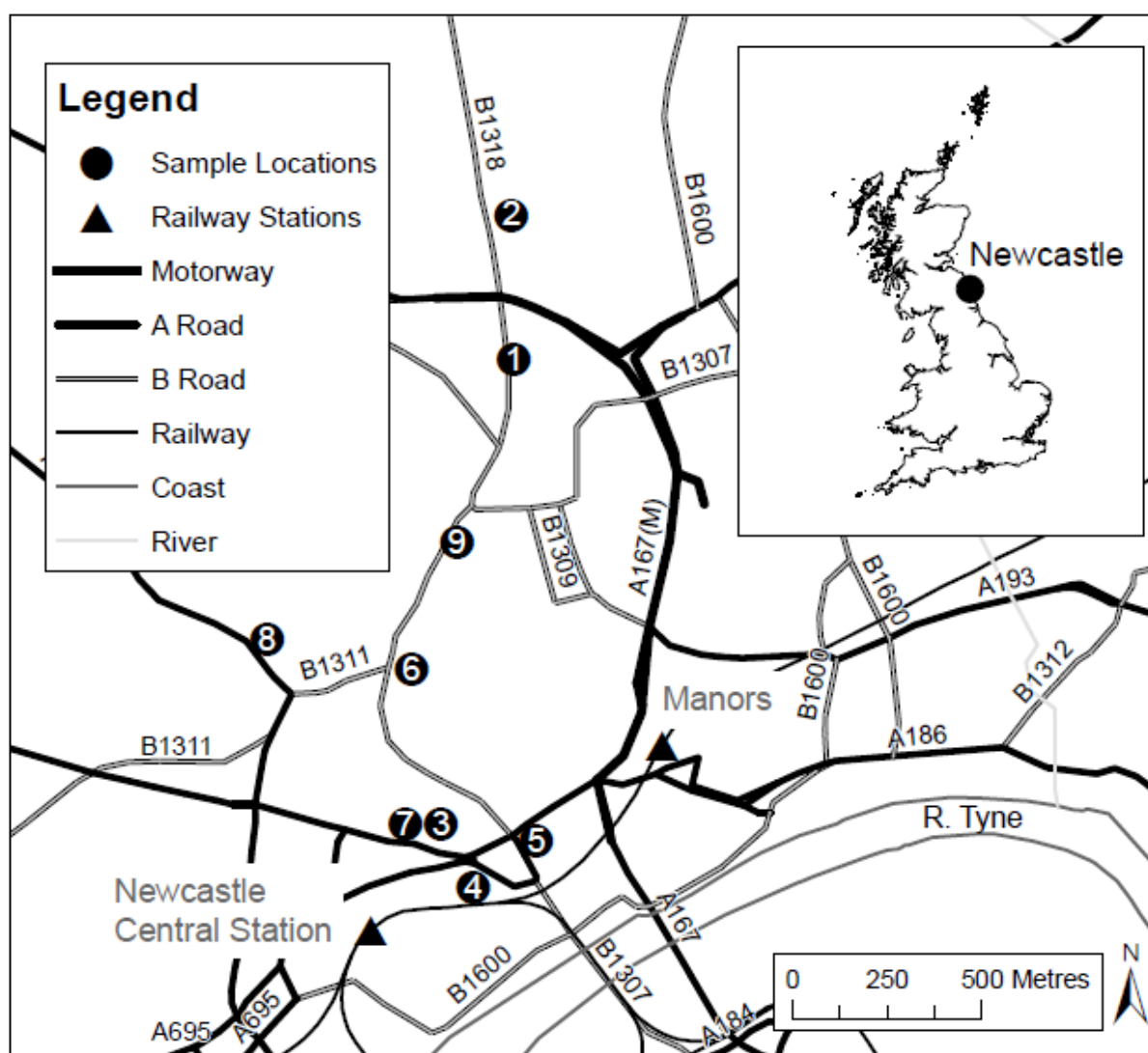


Figure 5.1: Map showing sampling points for the urban road dust

5.3 Results and Discussion

5.3.1 Quality Control

As ICP-MS can suffer from molecular interferences below 80 amu it is necessary to determine its mode of operation i.e. standard or collision / reaction cell mode. On that basis ^{75}As , ^{63}Cu , ^{60}Ni and ^{66}Zn were determined using a CCT mode whereas ^{111}Cd and ^{208}Pb were determined in standard mode. Calibration curves were prepared for the six PTEs under investigation in this study; based on a calibration range from 0 - 400 ppb with 8 data points

Table 5.1: Sample location, driving style and traffic volume

Site number	Location	No of vehicles / day*	Driving Style	Description/sources	Possible receptors
1	Robinson Library, Claremont Road	14,091	Constant Speed	North of City Centre air quality Management area (AQMA). Entrance to Claremont bridge (over the Great North Road B1318) directly opposite entrance to Robinson library. Ivy (<i>Hedera sp.</i>) forming a semi protected area in which soil/dust can accumulate. Matrix comprising soil from adjacent landscaped area and curb-side dust.	Busy pedestrian thorough fair with cyclist
2	Brandling Park, Forsyth Road	28885	Constant Speed	North of City Centre AQMA. Park adjacent (to the east) of the Great North Road B1318. Sample taken from a rectangular seating area. Matrix comprising soil from adjacent landscaped area and general urban inputs; sloppy sediment overlain by leaf litter.	Urban parkland. Receptors include dog walkers, pedestrians and those using the site as a general recreation area
3	Grainger Street opposite St John's Church	3338	Stop and Start	Sample collect from corners either side of 3 doorways and recessed areas between two buildings. Matrix: street dust and 'rubbish' (cigarette ends, litter & other detritus of plant and animal origin).	Busy pedestrian route to and from station. Busy with vehicular traffic.

4	Bolbec Hall, Westgate Road	8629	Stop and Start	Sample taken along base of lowest stone step. Matrix: street dust, sediment and 'rubbish'(cigarette ends, litter & other detritus of plant and animal origin).	Busy with vehicular traffic. Critical receptors pedestrians.
5	St Nicholas Church, St Nicolas Street	9873	Stop and Start	Sample taken along edge of building adjacent to Nicholas Road and either side of main doorway on St Nicholas Place.	Adjacent to busy pedestrian route. Busy with vehicular traffic.
6	Blacket Street	1075	Stop and Start	Sample taken in 'tunnel' (Eldon square shops above) from block paved area either side of the main road. Road access restricted to buses and taxis.	Adjacent less than 2 m away to busy pedestrian route.
7	Westgate Road opposite County Court	7752	Stop and Start	Samples collected from the edge of the busy road opposite to a pub. Matrix: Dust particles blown to the edges of the road	Adjacent to busy pedestrian route. Busy with vehicular traffic.
8	St James's Park, Strawberry Street	5063	Stop and Start	Sample taken along the edges of the road opposite St James Park and busy with vehicular traffic.	Adjacent to busy pedestrian route, especially during football match.
9	Percy Street, opposite Haymarket bus station.	1815	Stop and Start	This sample was collected from corners of the building directly opposite the Hay market bus station.	Receptors here are the pedestrian and those queuing for buses.

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typical correction coefficients (r^2) for all elements were in excess of 0.99. The dust certified reference material (BCR 723) was digested using the microwave protocol described in 3.2.3 and 4.2.6 and then its PTE content determined using ICP-MS. As the CRM has no certified values for the PTEs under investigation in this study only its indicative values could be used. The results are shown in Table 5.2. Excellent agreement was obtained with the known indicative values (Cd, Ni, Pb and Zn); no values were available for As and Cu.

Table 5.2: Analysis of PTE content of dust certified reference material (BCR 723) using microwave digestion-ICP-MS

Element	Indicative value (mg/kg)	Measured values (mg/kg) Mean \pm SD (n = 3)	
		Standard Mode	CCT Mode
As	NA	NA	10.3 \pm 2.1
Cd	2.5 \pm 0.4	2.4 \pm 1.1	NA
Cu	NA	NA	175 \pm 3.1
Ni	171 \pm 3	NA	171 \pm 3.5
Pb	866 \pm 16	867 \pm 2.3	NA
Zn	1660 \pm 100	NA	1602 \pm 3.7

5.3.2 Pseudo total PTE concentration

Dust samples were analysed using $< 250 \mu\text{m}$ particle size as this is the fraction that is most likely to adhere to hands and thus most likely to be involuntarily ingested (34). A summary of the overall data in the form of a box plot is shown in Figure 5.2. The mean concentrations of As, Cd, Cu, Ni, Pb and Zn are 6.4, 1.0, 132, 26, 992 and 421 mg/kg, respectively. A major outlier in the data occurs for Pb at site 5 (4000 mg/kg); outside the cathedral church of St. Nicholas and located on a major road artery through the city centre. Statistical evaluation of the data (normality test) indicates that majority of the elements display a normal distribution (p-values >0.05), except for Cd and Pb (Table 5.3). As a result of this normal distribution, the mean is shown for As, Cu, Ni and Zn while the median is used for Cd and Pb for non-parametric alternative (see Figures 5.2-5.8). It therefore appears that based on the normality test and coefficient of variation (CV) that the examined elements can be classified into two groups: Cd and Pb whose CVs are higher than 100 and the other PTEs (As, Cu, Ni and Zn) whose CVs are lower than 100 (35).

The concentrations of each of the elements across the samples are shown in Figures 5.2-5.8. In addition, global road dust concentrations of the PTEs under consideration have been

compiled from the literature and are shown in Table 5.4. In each case the determined concentration is compared with Soil Guidelines Values (SGVs) (63) or Generic Assessment Criteria (GACs) (64) (acknowledging the fact that these are based on a very prescribed set of scenarios) as well as a comparison with the literature. The results obtained for each element are discussed below.

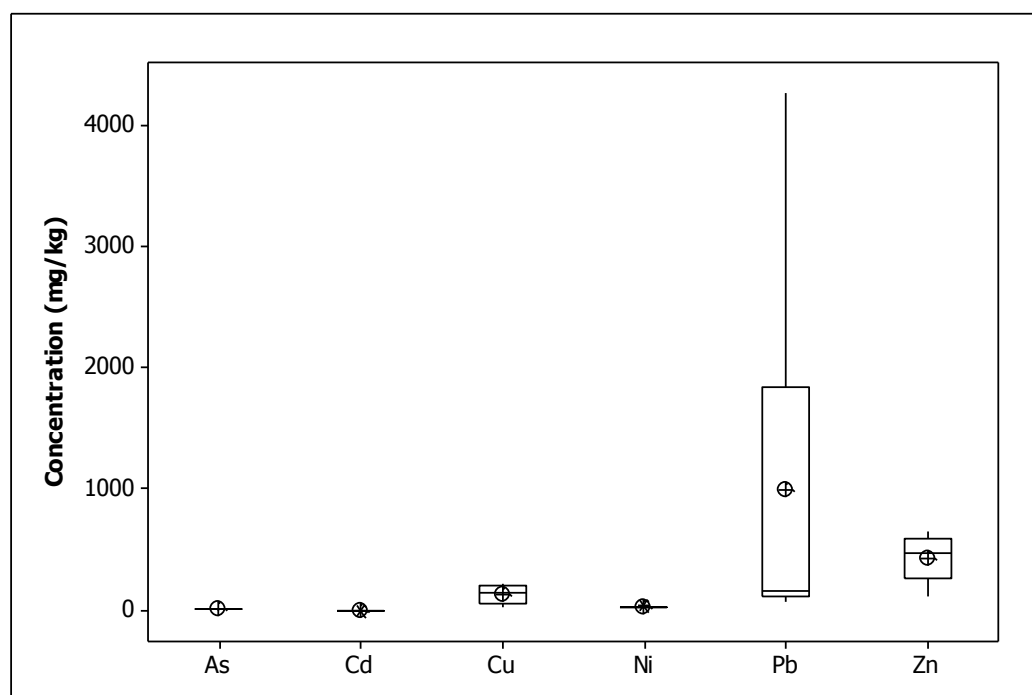


Figure 5.2: Box plot of total PTE concentration in street dust: *central solid line* median, \oplus mean, *box boundary* 25th and 75th percentile and *whiskers* 10th and 90th percentile.

Table 5.3: Normality test on the < 250 μ m size fraction of street dust

Elements	As	Cd	Cu	Ni	Pb	Zn
p-value	0.463	0.016	0.569	0.084	0.005	0.703
Cv	22.2	106.5	52.2	35.0	146.2	45.1

cv = coefficient of variation

Arsenic

The concentration of As in the road dust samples from Newcastle upon Tyne ranges from 4.4 to 8.6 mg/kg with an average value of 6.4 mg/kg (Figure 5.3). It can be seen that As concentration is highest in site 1 (8.6 mg/kg) which was collected in front of Robinson Library and lowest in site 2 and 3 (4.4 mg/kg) which were collected from Brandling Park and Grainger Street, respectively. These values are below the SGV for As for residential (32 mg/kg), allotment (40 mg/kg) or commercial (640 mg/kg) (65). Data for As concentration in urban dusts are relatively few in the literature, but in comparison to Kavala in Greece (13)

where the As concentration in road dust was determined with a mean concentration of 13.7 mg/kg, the concentration across the sites samples in this study are in reasonable accord.

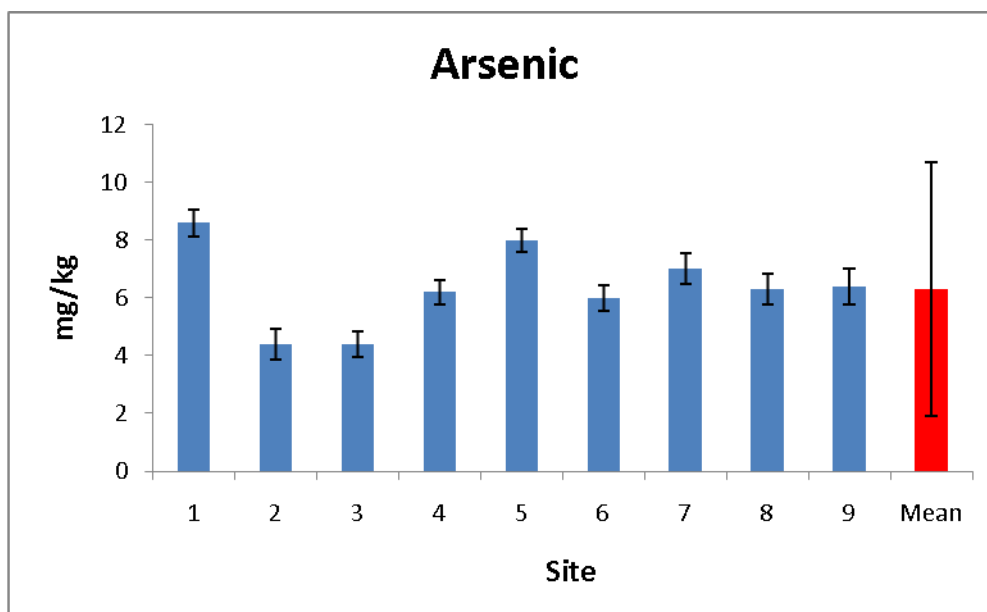


Figure 5.3: Pseudo total content of As in the <250 µm particle size fraction of dust sample collected from Newcastle city centre

Cadmium

The Cd concentration in the road dust of Newcastle upon Tyne varies from 0.13 – 1.6 mg/kg with an average value of 1.0 mg/kg and lowest among the elements studied (Figure 5.4). This concentration is very similar to that found in a typical soil (0.1 – 1.0 mg/kg) (34). The average Cd concentration is lower than the SGV for residential (10 mg/kg), allotment (1.8 mg/kg) and commercial (230 mg/kg) (65). The Cd concentration is highest in the sample from site 4 and lowest in sample from site 2. The global Cd concentration shows a large range of values from 0.2 to 72 mg/kg. The concentration of Cd in Newcastle upon Tyne city centre is greater than those cited for 4 cities: 0.9 mg/kg (Coventry (UK) (25); 0.32 mg/kg (Sweden) (41); 0.2 mg/kg (Kavala, Greece) (13); and, 0.37 mg/kg (Ottawa, Canada) (46) Table 5.4. The differences in Cd concentration reported in this study fall within the range reported in the literature across 26 cites globally (Table 5.4).

Copper

Figure 5.5 shows the variation of concentration of Cu in the sampled area. From the current study, the average concentration of Cu is 132 mg/kg with a range of 25.3 to 217 mg/kg. The average concentration (132 mg/kg) is greater than that found in a typical soil (5 - 20 mg/kg) (67). The highest concentration of Cu is found in site 4 and lowest in site 2.

Table 5.4: Global pseudo total PTE concentrations (mg/kg) in street dust

City/Country	As	Cd	Cu	Ni	Pb	Zn	Year of study	Reference
<i>Newcastle upon Tyne (UK)</i>	<i>6.4</i>	<i>1.0</i>	<i>132</i>	<i>26</i>	<i>992</i>	<i>421</i>	<i>2009</i>	<i>Present study</i>
Birmingham (UK)	-	1.6	467	-	48	534	2003	25
Coventry (UK)	-	0.9	226	-	47	385	2003	25
Lancaster (UK)	-	1.0 – 14.6	-	15 – 126	150 -	160 - 3725	1979	36
London (UK)	-	3.5	155	-	1030	680	1988	19
Manchester (UK)	-	-	113	-	265	653	2003	37
Aviles (Spain)	-	22.3	183	-	514	4829	2003	38
Madrid (Spain)	-	-	118	44	1927	476	1997	21
Paris (France)	-	1.7	1075	25	1450	840	2001	39
Oslo (Norway)	-	1.4	123	41	180	412	1997	21
Palermo (Italy)	-	1.1	98	14	544	207	2003	40
Sweden	-	0.32	79	12	53	220	2006	41
Various Cities (Bahrain)	-	72	-	126	697	152	1993	12
Athens (Greece)	-	1.8 – 4.3	-	-	65 – 259	75 - 241	1987	42
Kavala (Greece)	13.7	0.2	124	58	301	272	2009	13
Launda (Angola)	-	1.1	38	10	266	98	2005	43
Various Cities (Nigeria)	-	0.2 – 1.7	-	1 – 3	4 – 243	12 - 48	1984	18
Cincinnati, Ohio (USA)	-	-	253	-	649.7	-	1998	44
Honolulu, Hawaii (USA)	-	-	167	177	106	434	2000	45
Ottawa (Canada)	-	0.37	65.8	15.2	39.1	112.5	2001	46
Hermosillo (Mexico)	-	4.25	26.3	4.7	36.2	388	2007	47
Baoji (China)	-	-	123	49	408	715	2009	27
Beijing (China)	-	1.67	42	72	126	167	2007	48
Guangzhou (China)	-	2.4	176	23	240	586	2006	49
Hong Kong (China)	-	2.18	24.8	-	93.4	168	2001	4

Hong Kong (China)	-	-	110	28.6	120	3840	2003	50
Shanghai (China)	-	1.2	196.8	84	295	734	2008	2
Xian (China)	-	-	95	-	231	422	2006	51
Istanbul (Turkey)	-	1.0 – 6.7	47 - 407	10 – 66	61 – 383	226 - 1852	2003	24
Kayseri (Turkey)	-	2.53	36.9	44.9	74.8	112	2006	52
Sivas (Turkey)	-	2.6	84	68	197	206	2003	53
Yazgat (Turkey)	-	3.0	38	77	69	-	2005	54
Aman (Jordan)	-	3.1 – 11.2	66.5 - 350	43 – 88	210 – 1131	166-410	2007	55
Aqaba-Shuna (Jordan)	-	5	-	40	79	79	2004	3
Aqaba (Jordan)	-	1.9 – 2.9	21 - 56	51 - 115	93 – 212	103 - 160	2007	55
Karak (Jordan)	-	-	11.3	4.2	11.2	13.1	2004	56
Dhaka (Bangladesh)	-	-	46	26	74	154	2006	57
Kuala Lumpur (Malaysia)	-	3.0	-	-	2466	344	1989	58
Cuenca (Equador)	-	0.6 – 1.4	-	-	19 – 970	44 - 1018	1990	59
Islambad (Pakistan)	-	5.0	52	23	104	116	2009	60
Calcutta (India)	-	3.12	44	42	536	159	1999	61
Taejon (Korea)	-	-	47 - 57	-	52 – 60	172 - 214	1998	62

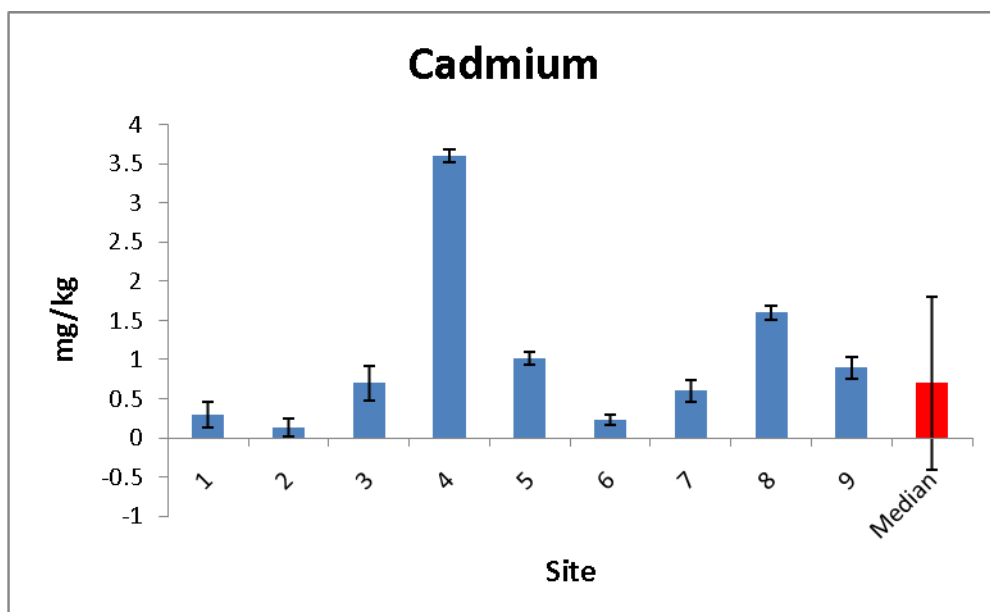


Figure 5.4: Pseudo total content of Cd in the <250 μm particle size fraction of dust sample collected from Newcastle city centre

The global concentration of Cu as reported in Table 4 varies from 11.3 - 1075 mg/kg.

Among the 41 places reported, 9 places have higher and 23 places have lower concentration of Cu than in this study.

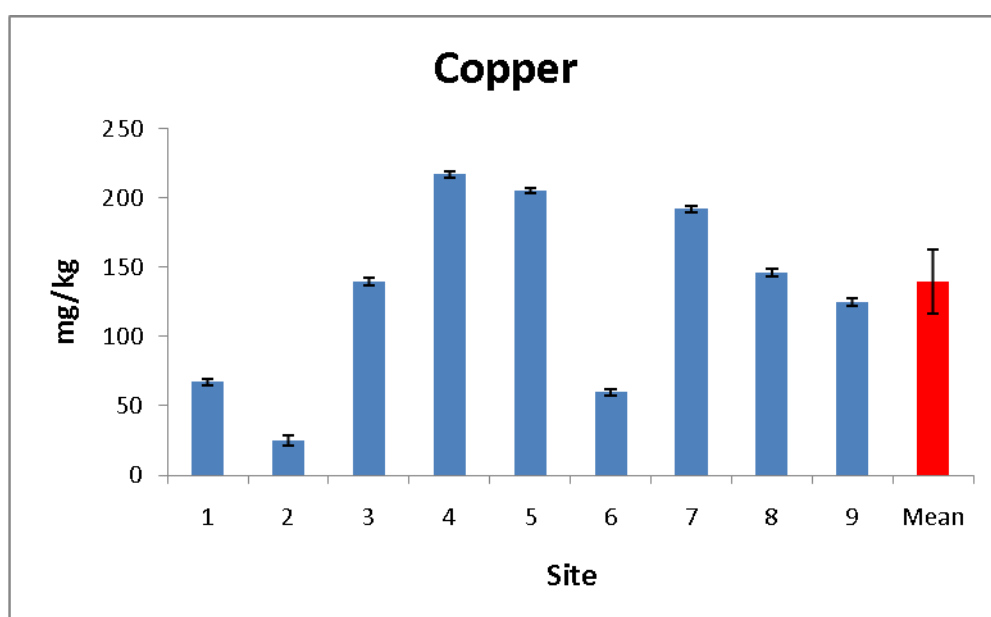


Figure 5.5: Pseudo total content of Cu in the <250 μm particle size fraction of dust sample collected from Newcastle city centre

Nickel

The concentration of Ni in the dust samples, for all the sampled sites, varies between 13.7 – 46.1 mg/kg with an average concentration of 26 mg/kg (Figure 5.6). The highest Ni concentration of 46.1 mg/kg is found in site 3 and the lowest value of 13.7 mg/kg was found

in site 2. The value of the Ni concentration measured was found to be below the SGV for residential (130 mg/kg), allotment (130 mg/kg) and commercial (1,800 mg/kg) (68). Of the 41 cities of the world reported in Table 5.4, 17 of the cities have higher Ni concentration than the ones determined in this study (and 9 with lower concentrations).

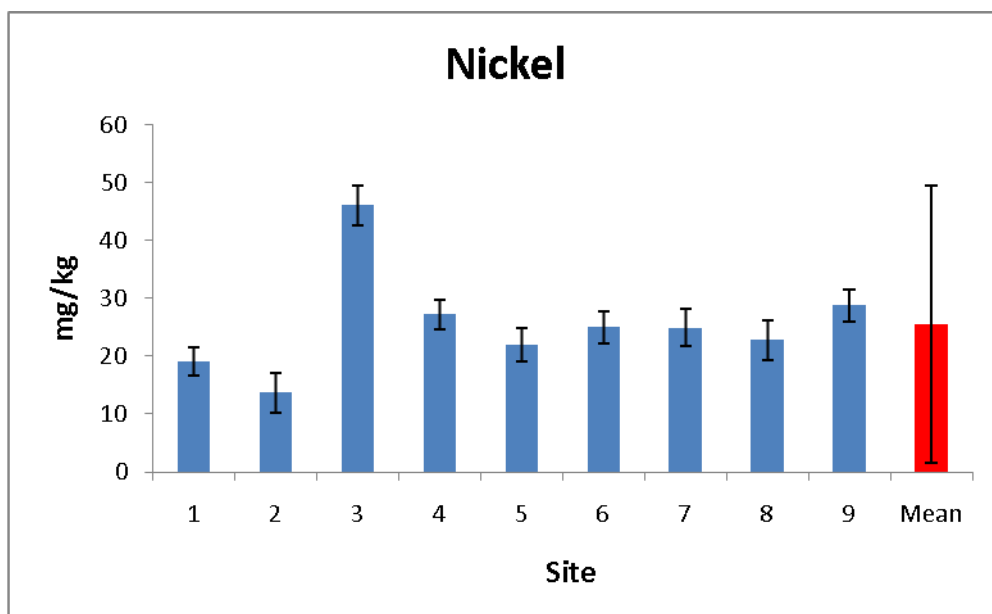


Figure 5.6: Pseudo total content of Ni in the <250 μm particle size fraction of dust sample collected from Newcastle city centre

Lead

The variation in Pb concentration in the present study is large; Pb concentration varies in the range 70.2 to 4261 mg/kg with a mean value of 992 mg/kg (Figure 5.7). The highest concentrations of Pb are observed at sites 4, 5 and 7 where the concentrations are 2363, 4261 and 1312 mg/kg, respectively. These areas are among the sampling sites with the highest traffic volume. In contrast the lowest concentration of Pb was found at site 2 (Brandling Park) where the traffic loading was the highest. This low Pb concentration is perhaps as a result of the driving style i.e. constant velocity, and the distance of the park from the road. The mean concentration of Pb in the road dust is higher than the SGV for residential / allotment (450 mg/kg) and commercial (750 mg/kg) (69). The concentration of Pb globally varies from city to city and is within the range 4 to 15,000 mg/kg (Table 5.4). Of the 41 cities shown in Table 6.4, only 4 places have their Pb concentration greater than in the present study while the majority (i.e. 35 places) have lower Pb concentrations in their street dust.

Zinc

The Zn concentration in the road dust samples ranged from 111 to 652 mg/kg (Figure 5.8)

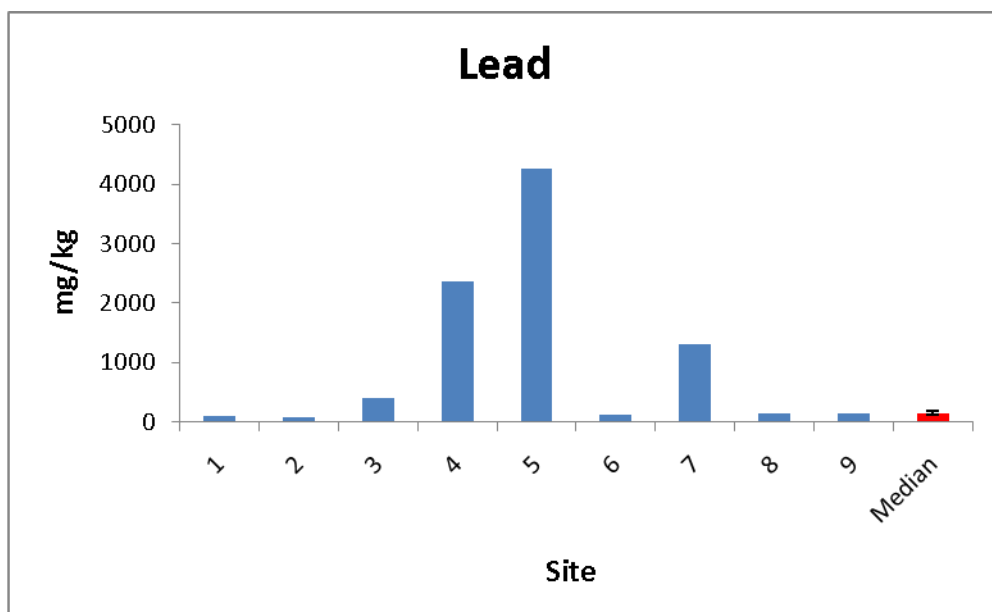


Figure 5.7: Pseudo total content of Pb in the <250 μm particle size fraction of dust sample collected from Newcastle city centre

average value of 421 mg/kg which is higher than the concentration of Zn in soil (10 - 50 mg/kg) (67). The average value of Zn in the street dust in this study is higher than the GAC value for residential/plant uptake (320 mg/kg) and lower than the industrial value (188000 mg/kg) (64).

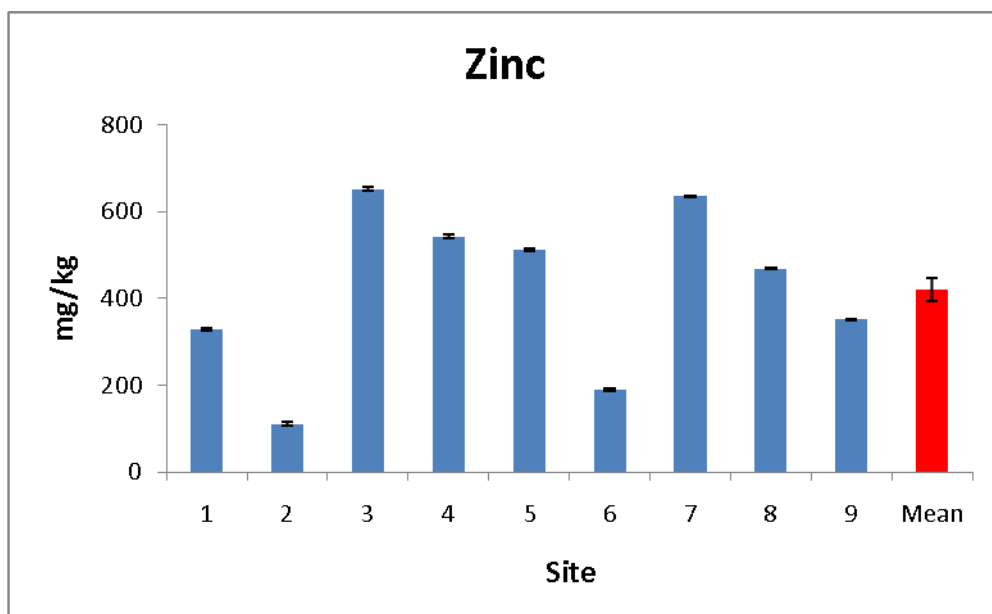


Figure 5.8: Pseudo total content of Zn in the <250 μm particle size fraction of dust sample collected from Newcastle city centre

The global concentration of Zn varies in the range of 13 to 4829 mg/kg (Table 5.4) with 10 places having higher Zn concentrations and 25 places lower than in the present study.

5.3.3 PTE concentration/traffic volume

Some researchers (70-71) have suggested a direct relationship between PTE levels and traffic volume in the roadside environment while others (70) have demonstrated that driving style may be more influential in affecting metal concentration. The results from this study suggest that there appears to be no straightforward correlation between traffic volume and PTE concentration. In general, higher PTE concentrations are found at sites where the predominant driving style is stop/start (i.e. intersection and traffic lights); these locations form either a major route to the city centre or are within the city centre and thus subject to frequent traffic congestion. In contrast, the lower PTE concentrations were from samples with high traffic volumes i.e. 14091 and 28885 vehicles per day at site 1 and site 2, respectively (Table 5.1). At these sites the traffic is generally a constant flow. In addition, sample site 6 has the lowest volume of traffic but a higher PTE concentration than those with the highest traffic flow (sites 1 and 2). This suggests that driving style has the most significant effect on metal contamination in road side dust compared to traffic volume. Graphical relationship between the traffic volume and pseudo total concentration of urban road dust is shown in appendix F.

5.3.4 Inter-element relationship in road dust

In order to investigate any inter-element relationship in the road dust samples correlation analysis was performed (Table 5.5). From the matrix generated (Table 5.5) it is evident that some correlation exists between most PTEs investigated, except As. Strong positive correlations exist between Cu and Cd (0.680), Pb and Cu (0.736), Zn and Cu (0.856) (Table 5.5). These significant positive correlation values may indicate that road dust contamination by these PTEs (Cd, Cu, Ni, Pb and Zn) originated from common sources (e.g. automobiles) while the lack of correlation between As and the other PTEs may be indicative of multiple or independent sources. The moderate correlation value of 0.404 between As and Pb may imply at least one common source e.g. traffic related.

5.3.5 Bioaccessibility of PTEs in urban street dust

The oral bioaccessibility of PTEs from the dust reference material (BCR 723) and the urban dust samples were assessed using the *in vitro* PBET procedure. The percentage bioaccessible fraction (% BAF) was calculated using the equation 4.1.

Table 5.5: Inter-element correlation matrix for street dust.

Metal	As	Cd	Cu	Ni	Pb	Zn
As	1.000					
Cd	0.025 (0.949)	1.000				
Cu	0.282 (0.462)	0.680 (0.044)	1.000			
Ni	-0.372 (0.325)	0.152 (0.697)	0.342 (0.368)	1.000		
Pb	0.404 (0.281)	0.427 (0.252)	0.736 (0.024)	-0.047 (0.905)	1.000	
Zn	0.135 (0.729)	0.437 (0.239)	0.856 (0.003)	0.629 (0.069)	0.447 (0.228)	1.000

Numbers in bracket represents the p-values

In order to assess the oral bioaccessibility (BARGE) procedure the CRM (BCR 723) was analysed and the results are shown in Table 5.6. A mass balance approach was adopted to assess the overall recovery of the six PTEs after *in vitro* BARGE procedure. By summing the ‘gastric + intestinal’ stage II fraction with the ‘residual’ stage III fraction allows the total recovery of the procedure to be determined. Based on the pseudo-total, as determined using the microwave digestion protocol, recoveries between 83 to 98% were obtained.

The BARGE methodology, as described above, was applied to all the dust samples from the Newcastle city centre to assess the oral bioaccessibility. A summary of the data is shown in Table 5.7 indicating the minimum, median and maximum concentration extracted using either gastric only (stage I) or gastric + intestinal (stage II) for all 6 elements investigated from the 9 sampling positions. In addition, for each element and stage the worst case scenario for the %BAF is shown (i.e. for the maximum determined PTE concentration at each stage) Table 5.7 It is noted that %BAF varies across the PTEs studied as well as the individual dust sample locations (see appendix C). The difference in bioaccessibility between the elements is most likely to be as a result of the different chemical forms in which the PTEs are bound to the dust constituents. Previous studies have shown that the bioaccessibility of some PTEs in the stomach phase is higher than in the intestinal phase but in this work, it is apparent (see

appendix C) that the gastric + intestinal stage always exhibited the highest %BAF as shown in the boxplot Figure 5.10.

It is noted (Figure 5.10) that Cd and Zn have a relatively high bioaccessibility (i.e. mean values > 45%) in both the 'gastric' and 'gastric + intestinal' fractions. In addition, it has been reported, that PTEs from anthropogenic sources are generally more soluble in the gastrointestinal environment and thereby more bioaccessible (72). It is therefore concluded that Cd and Zn are most likely derived from anthropogenic sources whereas the lower mean values (i.e. < 30% bioaccessible) for As, Cu, Ni and Pb may be indicative of mixed sources of origin i.e. a combination of both anthropogenic and natural origin. It should however be noted that bioaccessible values for As, Cu, Ni and Pb are wide ranging with samples having bioaccessible values over 45% (Figure 5.10).

5.3.6 Bioaccessibility of PTEs in urban street dust by TDI or MDI

As earlier discussed in section 4.3.5, the bioaccessibility of dust sample can be estimated by calculating the mass of dust that a child would require to ingest to reach the estimated TDI or MDI for each of the PTEs investigated. The values of the TDI are shown in Table 5.8 and are based on a 10 kg child, while the values for the MDI are based on a child aged between 5-6 years of age and which corresponds to a weight of 20 kg. On the basis of the recommendations discussed in section 4.3.5, the amount of PTE ingested from the dust sample was calculated based on 50 g/day (geophagy), 1 g/day (soil-pica) and 0.1 g/day (guideline value based on unintentional ingestion). The values obtained were compared with the TDI (or ID_{oral} in the case of As) and MDI values to assess the risk of the PTE to the child. From the results for a child with geophagy behaviour the levels of all PTEs are exceeded, except for Zn which is below the MDI. In contrast for a child with pica behaviour (1 g/day) only one PTE exceeds the TDI value i.e. Pb; in addition, for As, the ID_{oral} value and the MDI values are exceeded. None of the PTEs investigated exceed the guidelines values for this type of sample i.e. based on the unintentional consumption of 0.1 g of dust. This calculation assumes ingestion (oral) as the only means of exposure ignoring other routes such as inhalation which might be very useful route of exposure to dust samples.

Table 5.6: Indicative, pseudo-total, stage related bioaccessible and residual fractions of PTEs in BCR 723.

Element	Indicative value	Pseudo-total metal (mg/kg)	<i>In-vitro</i> gastro-intestinal extraction, mg/kg						
			Stage I (Gastric digest)		Stage II (Gastric + Intestinal digest)		Stage III (Residual digest)	Total metal II + III	
			Mean \pm SD; (n = 3)	% BAF	Mean \pm SD; (n = 3)	% BAF	Mean \pm SD; (n = 3)	Mean \pm SD; (n = 3)	% Residual
As	NA	10.3 \pm 2.1	1.8 \pm 8.1	17.5	3.0 \pm 10.4	29.1	6.4 \pm 3.2	9.4 \pm 21.7	91.3
Cd	2.5 \pm 0.4	2.4 \pm 1.1	1.2 \pm 2.3	50.0	1.3 \pm 0.9	54.2	0.8 \pm 1.2	2.1 \pm 4.4	87.5
Cu	NA	175 \pm 3.1	40.8 \pm 4.9	23.3	71.5 \pm 4.5	40.9	96.2 \pm 5.3	167.7 \pm 14.7	95.8
Ni	171 \pm 3	171 \pm 3.5	38.7 \pm 5.2	22.6	59.7 \pm 5.4	34.9	105 \pm 2.3	164.7 \pm 12.9	96.3
Pb	866 \pm 16	867 \pm 2.3	96.4 \pm 83	11.1	123.8 \pm 13	14.3	595 \pm 15	718 \pm 111	82.8
Zn	1660 \pm 100	1602 \pm 3.7	527 \pm 5.5	32.9	683 \pm 7.2	42.6	886 \pm 23	1569 \pm 35.7	97.9

% BAF: stage related bioaccessibility, calculated as a fraction of the pseudo-total; **% Residual:** residual fraction calculated as a fraction of the pseudo-total; **NA** = not available

Table 5.7: Summary of Stage related bioaccessibility and residual fraction of PTEs in road dust.

Element	<i>In-vitro</i> gastro-intestinal extraction (mg/kg)								
	Stage 1 (Gastric digest)			Stage 2 (Gastric + Intestinal digest)			Stage 3 (Residual digest)		
	Minimum	median	Maximum (% BAF)	minimum	Median	Maximum (% BAF)	minimum	median	Maximum (% residual)
As	0.60	0.90	1.60 (18.6)	1.0	1.70	3.1 (36.1)	3.70	4.80	6.60 (76.7)
Cd	0.03	0.20	1.50 (41.7)	0.03	0.30	1.90 (52.8)	0.13	0.49	2.20 (61.1)
Cu	ND	7.50	65.60 (30.2)	1.60	23.30	74.10 (64.4)	19.5	102.20	145.50 (75.8)
Ni	0.70	2.90	5.90 (26.8)	2.1	6.0	8.80 (32.4)	9.30	18.30	40.50 (87.8)
Pb	0.04	33	1405 (32.9)	0	33.0	1586 (37.2)	52	138	2652 (62.2)
Zn	49.2	160	239 (37.6)	63.6	24.3	347(53.2)	51.70	211	335 (52.7)

% BAF: stage related bioaccessibility for the sample exhibiting the highest stage concentration, calculated as a fraction of that samples pseudo-total for gastric and intestinal phases; **% Residual:** residual fraction calculated as a fraction of the pseudo-total for the sample exhibiting the highest residual concentration; **ND** – not detected.

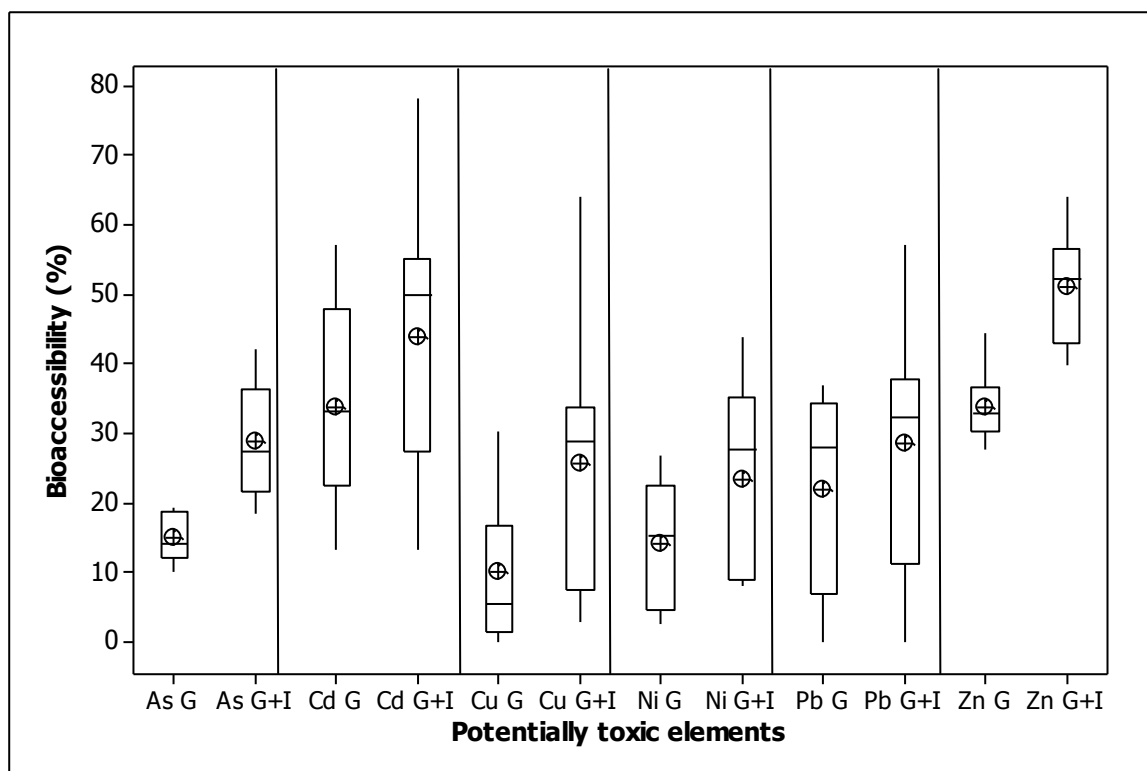


Figure 5.9: Box plot for oral bioaccessibility in road dust: *central solid line* median, \oplus mean, *box boundary* 25th and 75th percentile and *whiskers* 10th and 90th percentile.

However, it is concluded that the dust samples, in this study, do not constitute a potential risk for children based on daily visits to the areas studied.

5.4 Conclusion

The data presented supports the findings that PTEs from road dust have important inputs in the environment and need to be considered as part of any human health risk assessment. The mean concentrations of PTEs in the dust were as follows: Pb (992) > Zn (421) > Cu (132) > Ni (26) > As (6.4) > Cd (1.0) mg/kg. Statistical analysis such as correlation matrix and dendrogram shows that some of the PTEs have linkage which indicates common sources of pollutant. Cadmium and Zn are most likely derived from anthropogenic sources whereas the lower mean values (i.e. < 30% BAF) for As, Cu, Ni and Pb may be indicative of mixed sources of origin i.e. a combination of both anthropogenic and natural origin. In terms of the upper (90th) and lower (10th) percentiles, it is noted that Cd, Cu and Pb ('gastric + intestinal') individual values range in magnitude from 58-65 %BAF whereas As, Ni and Zn have a smaller %BAF range (25-35%). In addition, the bioaccessible concentration is considered in terms of the ingestion rate for a 10 kg child (i.e. in line with the tolerable daily intake, TDI, for Cd, Cu, Ni, Pb and Zn and the calculated ID_{oral} for As) (Table 5.8).

Table 5.8. Amount (µg) of PTE ingested from the sampled urban road dust calculated from the content of PTEs (mg/kg) and assumptions of daily soil (soil + outdoor settled dust) ingestion rates of 50 g (soil-geophagy), 1 g (soil-pica) and 0.1 g (guideline value based on unintentional consumption)(73). Particle size <250 µm, Tolerable daily intake (TDI) values and mean daily intake (MDI) for a child weighing 10 kg for TDI and 20kg for MDI are also presented.

Element	50 g/day ingestion rate	1 g/day ingestion rate	0.1 g/day ingestion rate	Bioaccessible concentration+ (g / day)	TDI ^a µg/day	MDI µg/day
As	315	6.3	0.6	0.03	3*	5 ^b
Cd	35	0.7	0.1	0.02	5	28.7 ^e 13.4 ^c
Cu	7000	140	14	0.74	1400	7000 ^e
Ni	1245	24.9	2.5	0.09	500	130 ^d
Pb	7650	153	15	15.9	36	N/A
Zn	23450	469	47	3.50	5000	27000 ^e

+ based on the maximum bioaccessible concentration using either the ‘gastric’ or ‘gastric + intestinal’ phase; in accordance with the TDI (ID_{oral}) the calculation is based on a child weighing 10 kg.

* oral index dose (ID_{oral}) value of 0.3 µg kg⁻¹ bw day⁻¹ (74) and assuming a child weighing of 10 kg.

^a reference (75); ^{b-d} references (76-78); ^e reference (64); N/A = not available.

The results range between 0.02 and 15.9 g / day. In all cases, except for Pb, the bioaccessible concentration is significantly below the guideline values based on unintentional consumption (0.1 g / day). On that basis use of the bioaccessible concentration offers an alternate basis for assessing risk to humans

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Chapter Six: Influence of particle size on the distribution of platinum group elements (PGEs) in urban street dust/sediments

6.1 Introduction

The PGEs comprise iridium (Ir), osmium (Os), palladium (Pd), platinum (Pt), rhodium (Rh) and ruthenium (Ru). These elements are all transition metals lying in the d-block (Group 8, 9 and 10 and period 5 and 6). Platinum and Pd are found in their pure state in nature (1). The other four elements Ir, Os, Rh and Ru occur as alloys of Pt and Au (2). Platinum group elements are mined in South Africa, Siberia and Sudbury, Ontario. The concentration of PGEs in the lithosphere is among the lowest, with the average estimated to be in the range of 0.001–0.005 mg/kg for Pt; 0.015 mg/kg for Pd; 0.0001 mg/kg for Rh; 0.0001 mg/kg for Ru; 0.005 mg/kg for Os; and 0.001 mg/kg for Ir (3, 2, 4). Worldwide production of PGEs has been steadily increasing since 1970. This reflects the growing worldwide use of PGEs (5). Of the six PGEs, the ones of interest for this study are Pd, Pt and Rh because of their use in the construction of catalytic converters used in the automobiles. The total worldwide supply in 1999 and 2000, as shown in Table 6.1, was 265 and 238 tonnes for Pd; 156 and 164 tonnes for Pt; 14.9 and 16.2 tonnes for Rh; respectively (6). In 2001 the highest published value for Pt in road dust was 2.252 mg/kg (7) and that of Pd was 0.556 mg/kg (8). The use of PGEs, reported in literature, is a cause of concern because relatively little is known about the mobility, toxicity and bioaccumulation processes of PGEs (9).

Platinum group elements have various applications one of which is their use in the construction of catalytic converters. The properties of PGEs which makes them suitable to be used as catalytic converter include: - (i) outstanding catalytic properties (ii) resistance to chemical attack (iii) stable electrical properties (iv) high corrosion resistance (v) low coefficient of thermal expansion (vi) high melting point (vii) high mechanical strength. Platinum group elements released from the catalytic converters are primarily bound to aluminium oxide particle (10, 11). They were until recently, regarded as inert elements but recent studies have shown that they may be soluble and quite reactive (12).

The main emissions of automobile engines are N_2 , CO_2 and H_2O . These emissions are mainly non harmful to human health however, because combustion is never perfect, smaller amounts of more harmful emissions are also produced namely carbon monoxide (CO), hydrocarbons (HC) or volatile organic compounds (VOCs) and oxides of nitrogen (NO_x). These gases are the largest source of ground level ozone which is responsible for smog formation, respiratory

Table 6.1: PGE supply by application (worldwide) (6)

Application	1999 (kg)	2000 (kg)
Palladium		
Autocatalysts	161,170	139,480
Dental	31, 500	24,700
Electronics	56,100	58,600
Other	16,600	15,000
<i>Total demand (Pd)</i>	265,000	238,000
Platinum		
Autocatalysts	33,600	38,000
Jewellery	79,400	83,300
Industrial	38,400	41, 400
Investment	5,100	1,420
<i>Total demand (Pt)</i>	156,500	164,000
Rhodium		
Autocatalysts	12,530	13,760
Chemical	964	992
Electronics	170	170
Glass	851	1,050
Other	312	312
<i>Total demand (Rh)</i>	14,900	16,200

Problems and plant life damage. The UK National Atmospheric Emissions Inventory (NAEI) report reveals that road traffic is the largest emission source of these pollutants and dominates UK emissions in 2007 contributing 53% of the total (13). Air quality problems experienced today in the UK are caused by pollution from road transport (14) which is being addressed by the UK National Air Quality Strategy (15). It is on this background that catalytic converter was developed to convert the three main regulated emissions gases to harmless products. The catalytic converter was made compulsory for all new cars coming into UK in 1991 therefore most modern cars are fitted with a three way catalytic converter. The three way refers to the three regulated emissions it helps to reduce-CO, unburnt HC and NO_x. The converter uses two types of catalyst: the reduction and oxidation catalyst. The Pd and Pt are used as oxidation catalyst to oxidise CO and HC while Rh is used as a reduction catalyst to reduce NO_x (16, 17). While the three way catalytic converters (Pd-Pt-Rh) significantly reduces up to 90% gas emissions produced during gasoline combustion (11, 18, 19) they may at the same time create serious environmental problems. This situation is due to the deterioration of the surface abrasion of the catalytic converter thus releasing the PGEs adsorbed in small particles

into the environmental compartments of air, soil and water (19). Several authors have linked increased concentrations of PGEs in our roadside environment to increases in the number of vehicles fitted with catalytic converters thereby causing environmental pollution (18, 20-25).

The trends over time in Pd and Pt used by application, for Europe are listed in Tables 6.2 and 6.3 (6). The growing demand for Pd in Europe is largely in response to the introduction of Euro Stage III legislation in January 2000, i.e. the Pd-rich catalysts can meet stricter emission limits for petrol-fuelled vehicles, resulting in a shift away from Pt-based technology (6).

Table 6.2: Palladium demand by application in Europe (kg) (6)

Palladium demand	1992 (kg)	1994 (kg)	1996 (kg)	1998 (kg)	2000 (kg)	2002 (kg)
Autocatalyst	1,130	7,370	24,258	38,658	51,175	38,690
Chemical	2,100	1,700	1,840	1,840	2,690	1,990
Dental	8,500	7,230	7,230	5,950	3,120	1,280
Electronics	5,950	7,230	8,500	7,660	7,370	3,120
Jewellery	992	851	851	1,420	1,280	990
Other	425	709	567	709	567	425
Totals (Pd)	19,100	25,100	43,200	56,300	66,200	47,800

Table 6.3: Platinum demand by application in Europe (kg) (6)

Platinum demand	1992 (kg)	1994 (kg)	1996 (kg)	1998 (kg)	2000 (kg)	2002 (kg)
Autocatalyst	16,158	16,916	14,033	14,649	16,770	32,850
Chemical	1,420	1,420	1,700	1,700	2,410	2,980
Electrical	851	709	709	1,280	2,270	1,840
Glass	425	851	1,130	709	709	280
Investment: small	992	1,276	142	142	0	0
Jewellery	2,410	2,840	3,540	4,540	5,670	4,820
Petroleum	567	709	425	425	284	425
Other	1,560	1,840	2,130	2,410	2,840	4,250
Totals (Pt)	24,400	26,500	23,800	25,800	30,900	47,400

Apart from catalytic converters, additional major uses of PGEs are in the glass, chemical, electrical, electronics and petroleum industries, the manufacture of jewellery, in medicine as cancer treatment drugs, and in dentistry as alloys.

6.1.1 Accumulation and mobility of PGEs

Research has shown that PGEs could become available to plants and especially to humans and livestock, who consume plants growing on a contaminated soil (26). Elevated and continuously increasing Pd and Pt levels were described for roadside grass samples, (27, 28).

The availability of PGEs to plants depends on their mobility and these elements become

mobile under acidic soil water conditions, a fact which increases their uptake by plants (1). PGEs emitted into the environment, may form soluble compounds able to be absorbed by plants, thus creating the possibility for their presence in the food chain. Catalyst converter emitted PGEs, may undergo rapid transformations in the environment, and subsequently behave similarly to soluble PGE salts (21). Hoppstock and Sures 2004 (29) in their review demonstrated biological availability of soluble and particle bound PGEs to plants and animals. Laboratory studies with mussels exposed to road dust revealed an increasing biological availability of PGEs in the following order: Rh > Pt > Pd (30). Similar results were obtained by Schafer and Punchelt 1998 (31) when demonstrating that plants can assimilate Pd, Pt and Rh. Tankari et al. 2007 (32) found that Pd and Rh concentrations increased with the time of plant exposure to PGE pollution.

6.1.2 Health risk effects of PGEs

The health effect of PGEs toxicity is exemplified by Pt. Platinum was believed to be chemically inert. However, this was not true as recent evidence suggests that Pt in the environment can be ionized into forms that are environmentally and biologically active (12). Platinum group elements which are released from catalytic converters are primarily bound to aluminium oxide particles (10). Up to 36% of these particles have a size <3 µm (33), and therefore reach lung alveolaries. Platinum in road dust can be solubilized, and enters the waters, sediments, soils and the food chain. Certain Pt compounds are also known to be cytotoxic and have mutagenic and carcinogenic effects which will have some effects on microorganisms at very low concentrations (5, 34). In addition, some Pt complexes can bind to N and S in proteins producing a reduction in enzymatic activity (6). Though initially automobile emitted PGEs were thought of as being inert biologically, recent studies have shown the biological availability of not only soluble, but also of particle bound PGEs, to plants and animals (35, 30).

Adverse occupational health effects following exposure to complex salts of Pt were first observed in 1911 in a photographic studio (1). Studies conducted on precious metal workers in four British Pt refineries revealed that 52 out of 91 persons had symptoms of sneezing, wheezing and shortness of breath (36). Platinum compounds, especially the soluble salts, such as ammonium tetrachloroplatinite(II) and ammonium hexachloroplatinate(IV) used in the production of industrial catalysts (37) are toxic, and chronic industrial exposure to them is

responsible for the development of a syndrome known as *Platinosis*, which is characterized by the respiratory and cutaneous hypersensitivity (34).

The first efforts towards understanding the PGEs risk effects was to analyze the body fluids for the basic three noble elements in people occupationally involved in PGEs manufacturing. Employees exposed during the production and recycling of Pt-based catalytic converters revealed Pt levels in urine and blood up to 100 times higher than those of non-exposed individuals (34). In general the Pt(II), Pt(V) and Pd (II) toxic effects on the cellular level are comparable to the toxic effects of Cd(II) and Cr(VI), sometimes even exceeding the damage induced by the above species of Cd and Cr (38).

Whereas numerous studies have concentrated on the heavy metal (e.g. Pb or Cd) concentration in the environment, relatively few studies focus on PGE (30). Following the potential health risk associated with PGEs and the accumulation and mobility of these precious metals in environmental matrices, this work focuses on PGE concentration in the environmental matrix of urban road dust and the influence of particle size on the distribution of these elements.

6.2 Experimental

6.2.1 Sampling and sample preparation

The sampling procedure is as described in 5.2.1 and sample location shown in Figure 5.1. Apart from the simplicity of using hand via sweeping, as opposed to a vacuum cleaner, part of this study was to investigate the PGE concentration according to particle size and the vacuum cleaner only samples particles finer than 250 μm thereby excluding the coarse particles needed for grain size analysis. Description of the sample sites are shown in Table 6.4. The dried samples were sieved through a plastic sieve of mesh size 2 mm to remove gravel, refuse and stones. Fractional size coarser than 2 mm was of limited importance when considering metal contaminants (39, 9). Only 3% of labile Pb is held in the 1000 – 2000 μm fractions and the remaining 97% labile Pb is in the 0 – 1000 μm fractions (9). It was on this basis that some of the samples (8, 14 and 15: the large ones) were fractionated into six size fractions with their sedimentological equivalent in parenthesis: 1000-2000 μm (very coarse sand), 500-1000 μm (Coarse sand), 250-500 μm (medium sand), 125-250 μm (fine sand), 63-125 μm (very fine sand) and <63 μm (silt and clay). All the samples (8, 9, 11, 13-15, 17-19) were passed through the 250 μm mesh size to separate between <250 and >250 μm . The dry

Table 6.4: Sample location/descriptions

Site number	Location	Description/sources	Receptors
8	All Saints Cemetery	A few meters west of Jesmond air quality management area (AQMA). Cemetery situated along the busy Jesmond Road. Matrix: Sample of soil/sediment taken from the base of the Cemetery wall immediately to the east of the Cemetery gate.	Busy pavement walkway and cemetery entrance.
9 (3)	Grainger Street opposite St John's Church	Sample collected from corners either side of 3 doorways and recessed areas between two buildings. Matrix: street dust and 'rubbish.'	Busy pedestrian route to and from station. Busy with vehicular traffic.
11 (4)	Bolbec Hall	Sample taken along base of lowest stone step. Matrix: street dust, sediment and 'rubbish.'	Busy with vehicular traffic. Critical receptors pedestrians
13 (5)	St Nicolas Church	Sample taken along edge of building adjacent to Nicolas Road and either side of main doorway on St Nicolas Place	Adjacent to busy pedestrian route. Busy with vehicular traffic.
14	St Nicolas Square	Sample taken in open paved square where sediment had accumulated in the uneven paving slabs. Matrix comprising soil from adjacent landscaped area and street dust.	Adjacent to busy pedestrian route. Busy with vehicular traffic.
15	Central Station	Sample taken under archway entrance to station adjacent to the taxi rank. Matrix: accumulated street dust.	Adjacent to busy pedestrian route. Busy with vehicular traffic.
17 (7)	Westgate Road opposite County Court.	Samples collected from the edge of the busy road opposite to a pub. Matrix: street dust particles blown to the edges of the road.	Adjacent to busy pedestrian route. Busy with vehicular traffic.
18 (8)	St James's Park	Sample taken along the edges of the road opposite St James Park busy with vehicular traffic. Matrix: accumulated street dust.	Adjacent to busy pedestrian route especially during football match.
19 (9)	Percy street opposite Haymarket bus station.	This sample was collected from corners of the building directly opposite the Hay market bus station. Matrix: accumulated street dust and 'rubbish.'	Receptors here are the pedestrian

Numbers in bracket represents the sample location in Figure 5.1

sieved samples were sub-sampled using cone and quarter prior to undergoing further analysis.

6.2.2 Instrument and reagents

Concentrated HCl and HNO₃ were obtained from Romil Limited Cambridge. A multi-element standard containing Ir, Pd, Pt and Rh was purchased from SPEXCertPrep (Middlesex, UK). Ultra pure water of conductivity 18.2MΩ-cm was produced by a direct Q™ millipore system (Molsheim, France). A road dust certified reference material was used (BCR 723 No 114) supplied by the institute for reference materials and measurements (Certified 2002, Revised 2008). Poly-prep chromatography columns and AG® 50W-X8 cation exchange resin 200 – 400 mesh size from Bio-rad laboratories Hercules Canada were used. An evaporating unit for Reacti-Therm™ heating models (containing Reacti-vap™ teflon® coated needles 4” (102 mm) x 19 gauge and Reacti-Therm™ heating module) and vortex mixer were from Fisher Scientific UK Ltd. (Loughborough, Leicestershire). Other instruments were specimen tubes made of soda glass with stopper, retort stand with clamps, glass measuring cylinder (A grade), volumetric flask (A grade) and eppendorf micro pipette. Dust samples were collected from locations across Newcastle city centre and local environs. ICP-MS measurements were carried out with an ICP mass spectrometer X series II (Thermo Electron Corporation, Cheshire, UK). All digestions were carried out using a Start D multiprep 42 high throughput rotor microwave digestion system supplied by Milestone Microwave Laboratory Systems UK. The weighing balance used was Explorer Ohaus model E406 00032 from Switzerland.

6.2.3 Preparation of cation exchange resin and separation columns

All plastic containers used were soaked in an acid bath for about one week prior to the preparation. They were rinsed with ultra pure water and allowed to dry before being used. 250g of AG 50 – X8 200 -400 mesh cation exchange resin was placed into a pre-cleaned one litre plastic container. 250 mL 6M HCl was added to the container and was shaken to allow mixing. This solution was allowed to stand overnight. The next morning the 6M HCl was decanted from the mixture and replaced by 250 mL 8M HNO₃. The new solution was shaken and allowed to stand overnight. The next morning the 8M HNO₃ was decanted from the mixture and replaced by 250 mL 6M HCl. This process of mixing and decanting 6M HCl and 8M HNO₃ was repeated three times. After the third time, the resin was finally stored in 250 mL 6M HCl and was ready for use (*C.Ottley, personal communication 2009*). The retort stands with the clamps were arranged such that the Poly-prep chromatographic column will

be held tightly and in a convenient position. The entire set up was placed in a well secured place to avoid shaking and other forms of interferences such as dust from external sources getting into the column. Once the column was set, 4 mL of freshly shaken resin was added to the column and the solution allowed to drain through. 10 mL of 6M HCl was added to the settled resin and the solution allowed to drain through, after which the solution was equilibrated using 15 mL of 0.5M HCl. A pre-cleaned acid washed specimen tube was placed beneath each column prior to the loading of the sample.

6.2.4 Microwave digestion and column separation for PGE analysis

The sample was digested using the microwave method, as outline in 2.2.3 and 3.2.6 except that 20 mL of aqua regia (HCl: HNO₃ 3:1 v/v), made from Romil acid, was used instead of 13 mL and the temperature raised to 200°C for 10 minutes. This is because catalyst-derived particles which carry PGEs are usually in a form difficult to digest (40). The filtrate from the microwave aqua regia digest was vortex mixed and sub-sampled by removing 4 mL from each sample and blank. The sample and the blank were evaporated to dryness under a stream of N₂ and heat. The residue was re-dissolved using 5 mL of 6M HCl, evaporated in stream of nitrogen and heat and then re-constituted using 2 mL of 0.5M HCl. After re-dissolving the re-constituted residue, the solution was added to the cation exchange column. The low affinity of PGE-anion complexes for the cation resin means that they begin to elute almost immediately. The eluent is collected in a pre- cleaned acid washed specimen tubes made of soda glass with poly stopper. To the same residue, further 2 mL of 0.5M HCl was added, vortex mixed and then poured to the cation exchange column. The eluent was collected in the same specimen tubes. A further 6 mL 0.5M HCl was added to the column and the eluent collected in the same specimen tubes. The process of washing the residue in the column with 2 mL and 6 mL of 0.5M HCl was repeated. Experiments have shown that this was sufficient to wash all PGEs of interest off the column while all major cations were retained (Al, Ca, Fe, K, Mg, Mn, Na and Ti) (41). The solution containing PGEs and other anion complexes from the column were evaporated to dryness under stream of N₂ and heat. To the dry residue was added two drops 16M HNO₃ to remove organics and then vortex mixed. This mixture was evaporated to dryness in a stream of N₂ and heat. The final residue was made up to 2 mL using 3% HNO₃, vortex mixed and stored in the fridge (4°C) for ICP-MS analysis.

6.2.5 Analysis of PGEs using ICP-MS

The analytical method adopted for this work follows that of Sutherland et al. 2007 (41). The

X series II ICP-MS was tuned using a 10 ppb solution of Li, Be, Bi, Ce, Co, In, Ba, Pb, Tl, U in 2% HNO₃ to verify mass resolution. The tuning was done in standard mode. The conditions for standard mode are shown in Table 6.5

Table 6.5: Operating conditions for ICP-MS

ICP-MS Conditions	Nebulizer flow rate L/Mins	Pole Bias (V)	Hexapole Bias (V)	Focus	Forward Power (W)	Resolution m/Δm
Standard Mode	1.0	12	20	30	1150	10000

Calibration standards ranging from 0.1 to 10 µg/kg prepared from a multi element standard (Ir, Pd, Pt and Rh), was used to calibrate the instrument and the calibration data are shown in Table 6.6. Masses 103, 105, 106, 108, 110, 194, 195, 196, 198 were measured in addition to masses 88, 89, 90, 95, 111, 114, 178 and 181 to correct for oxide interferences. Standard solutions of Hf, Sr, Y and Zr were run at the beginning of the analytical session to generate oxide production ratios that were used for on line corrections. Samples were washed out with 1% HNO₃ for three minutes between each analysis. Instrumental drift was monitored by regularly running standard element solution in between samples. Precision and accuracy were measured using certified reference material BCR 723 with certified concentrations of Pd, Pt and Rh. The soil samples and the blanks were diluted with an appropriate dilution factor. The samples and the blanks were analysed using ICP-MS with reference material analysed after every 8 samples.

Tale 6.6: Calibration Data for the PGEs

Elements	Isotopes	Calibration Equation $y = mx + c$	Correlation Coefficient r^2
Palladium	¹⁰⁵ Pd	$y = 20713.1x + 2.5 \times 10^{-4}$	0.9999
Platinum	¹⁹⁵ Pt	$y = 20345.4x + 5.3 \times 10^{-4}$	0.9999
Rhodium	¹⁰³ Rh	$y = 128047.4x$	0.9999

6.3 Results and Discussion

6.3.1 Isotope selection and interferences

Spectroscopic interferences are probably the largest class of interferences in ICP-MS and are caused by atomic or molecular ions that have the same mass-to-charge as the analytes of interest. The determination of PGEs using ICP-MS is associated with numerous of

interference problems. This spectroscopic interference, arising from major constituents of the sample, complicates PGE determination (42). It is particularly severe when analysing catalytic converter pollution products due to the common use of Sr and Zr substrate in the catalysts which generates unusually high and significant levels of oxide interferences on the PGE masses of interest (41). ICP-MS is used in the determination because of its multi-element capacity and the extent of the isotopic information one is able to produce.

The analytical isotopes ^{105}Pd , ^{195}Pt and ^{103}Rh were selected based on the natural abundances of the analytical isotopes and the ascertainment of relative abundances of the potential atomic and molecular interfering ions along with the resolution required to separate analyte masses from interfering masses (43). Palladium has 105, 106 and 108 isotopes with abundances of 22.3%, 27.3% and 26.5% respectively. The 106 and 108 suffers from isobaric monoatomic interference of Cd ion while ^{105}Pd does not suffer any monoatomic ion interference hence is the chosen isotope for analysis.

Platinum 195 was chosen as the preferred isotope for measurement because it has the highest abundance (33.8%) compared to the other isotopes. Platinum 194 has abundance of 32.9%.

Some of the interfering ions are quantitatively retained by the cation column relative to PGEs thus effectively separating them and causing reduced problems for example $^{87}\text{Sr}^{16}\text{O}$, $^{86}\text{Sr}^{17}\text{O}$ for ^{103}Rh and $^{89}\text{Y}^{16}\text{O}$ for ^{105}Pd (41). Hafnium and Zr behave as anion complexes (44, 45) and hence elute with the PGE from the cation column causing serious interferences. Oxides of these elements interfere on the Pd mass spectrum with respect to Zr and in the Pt mass spectrum for Hf. Oxides of these elements were reduced by the use of a nebuliser which maintains oxide generation levels below 0.05% of the total mass signal. Example, Zr signals of $> 10^6$ cps produces $^{90}\text{Zr}^{16}\text{O}$ signal of 500cps or less which can easily be corrected from PGE analyte signals that are normally $> 10,000$ cps. Interferences linked to other metals e.g. Cu, Zn and Pb, can be separated in the resolution mode of 4000 cps which is well below that for PGEs of 10,000 cps (46). Interferences not separated from instrumental manipulations and treatment stages were corrected mathematically by estimating the contribution of interfering species to the PGEs signal through the analysis of single element standard solutions of interferents as published in (10, 46, 47).

6.3.2 Quality control using certified reference material

Validation was performed by analysing dust reference material BCR 723. 0.5g of the CRM

was prepared using microwave digestion (see 2.2.3, 3.2.6 and 6.2.4) and the result of the analysis shown in Table 6.7. From the result, there is good agreement between the measured value and the certificate.

Table 6.7: Concentration of PGEs in Dust Reference Material BCR 723

Elements	Measured value (ng/g)	Certificate value (ng/g)
¹⁰⁵ Pd	4.8 ± 0.16	6.10 ± 1.9
¹⁹⁵ Pt	75.5 ± 1.16	81.3 ± 2.5
¹⁰³ Rh	8.6 ± 0.02	12.8 ± 1.3

6.3.3 PGE concentration in road dust

The PGEs was determined on the two size fractions >250 and <250 µm and the results shown in Table 6.8. From the results of the descriptive statistics (Table 6.9) and a Mann-Whitney test (Table 6.10), the median has a higher value in the < 250 µm fractions than in the > 250 µm even though there is no significant difference in Pd (p = 0.19), Pt (p = 0.15), or Rh (p = 0.08) concentration between the two fractions at 95% confidence interval. A comparative plot between the two fractions (Figure 6.1) shows that most of the data points fall within the <250 µm fractions when a 45° (1:1) line passes through the plot. On this basis the < 250 µm fraction was chosen and as the more conservative fraction in terms of determining the concentration of the PGEs and subsequent description of the data will be centred on this fraction.

Platinum, Pd and Rh concentrations in road dusts from Newcastle city centre are presented in Figure 6.2.

Table 6.8: Concentration of PGEs in >250 and <250µm (ng/g)

Site	>250 µm			<250 µm		
	¹⁰³ Rh	¹⁰⁵ Pd	¹⁹⁵ Pt	¹⁰³ Rh	¹⁰⁵ Pd	¹⁹⁵ Pt
8	2.73 ± 0.05	10.15 ± 0.25	10.78 ± 0.34	27.34 ± 0.14	52.16 ± 0.57	24.20 ± 0.74
9	8.83 ± 0.29	52.57 ± 0.71	26.59 ± 1.18	6.38 ± 0.31	49.78 ± 1.36	29.51 ± 0.19
11	28.93 ± 0.40	51.59 ± 0.75	356.73 ± 17.11	41.32 ± 0.49	203.68 ± 3.46	54.36 ± 1.60
13	5.72 ± 0.19	46.08 ± 1.70	18.11 ± 0.34	11.25 ± 0.38	166.38 ± 3.99	49.58 ± 0.25
14	1.88 ± 0.07	15.2 ± 0.06	8.09 ± 0.51	54.75 ± 0.14	37.96 ± 0.50	13.86 ± 0.03
15	0.08 ± 0.01	0.59 ± 0.01	5.12 ± 0.02	9.19 ± 0.20	2.70 ± 0.13	29.84 ± 0.47
17	1.37 ± 0.03	7.64 ± 0.09	6.07 ± 0.37	1.88 ± 0.04	9.71 ± 0.02	8.11 ± 0.63
18	5.01 ± 0.05	23.39 ± 0.61	1.33 ± 0.01	1.21 ± 0.05	8.30 ± 0.03	118.50 ± 3.33
19	3.23 ± 0.03	1.79 ± 0.04	18.89 ± 1.14	4.79 ± 0.01	186.92 ± 0.85	16.05 ± 0.23

The range of Pd, Pt and Rh concentrations from road dust are 2.70 – 203.7 ng/g, 8.1 – 118.5 ng/g and 1.2 – 54.8 ng/g respectively with mean concentrations of 79.8 ng/g for Pd and 38.2 ng/g for Pt and 17.6 ng/g for Rh. The mean value of Pd is significantly higher than those of Rh and Pt and this is not surprising as there is a widespread shift in the development of catalytic converter technology away from Pt towards Pd as the main catalytic component (21).

Table 6.9: Descriptive statistics for PGEs in the >250 and the <250µm size fraction of road dust samples (ng/g)

Elements	Mean		Median		SD		CV	
	>250	<250	>250	<250	>250	<250	>250	<250
¹⁰³ Rh	6.42	17.56	3.23	9.19	8.83	19.23	137.7	109.4
¹⁰⁵ Pd	23.22	79.8	15.24	49.78	21.4	81.9	91.8	102.8
¹⁹⁵ Pt	50.27	38.23	10.8	29.6	115.2	33.9	229.6	88.6

Samples 11, 13 and 19 exhibits the highest concentration of Pd contributing 28.4%, 23.2% and 26.1% respectively of the total PGE concentration. The highest concentration of Pt is found in sample 18 contributing 34.5% of the total concentration of PGE in the sampled area. The result obtained from Newcastle is compared to those of other cities in the world as shown in Table 6.11. Mean Pt concentration in Newcastle dust sample (38.2 ng/g) is comparable to those from Ioannina NW Greece (3.2-306 ng/g) (48), Scotland (13 – 335 ng/g) (24), Rome Italy (14.4 – 62.2 ng/g) (49).

Table 6.10: The Non parametric Mann-Whitney test results of >250 and <250 µm size fraction for the concentration of PGEs.

Elements	¹⁰³ Rh		¹⁰⁵ Pd		¹⁹⁵ Pt	
	>250	<250	>250	<250	>250	<250
Median	3.23	9.19	15.2	49.8	10.8	29.5
p-value	0.1449		0.1853		0.0774	

Mean Rh concentration (17.9 ng/g) in this study compare favourably with those of Bialystok, Poland (19.6 ng/g) (50), Perth in Austrelia (8.8-91.4 ng/g) (21), Ioannina NW Greece (6.1-64.6 ng/g). Mean Pd (79.8 ng/g) is similar to those reported in San Diego USA (38 – 280

ng/g) (51), Germany (1 – 146 ng/g) (52), Perth in Australia (58.1-440.4 ng/g) (21), and Goteborg in Sweden (80 ng/g) (7).

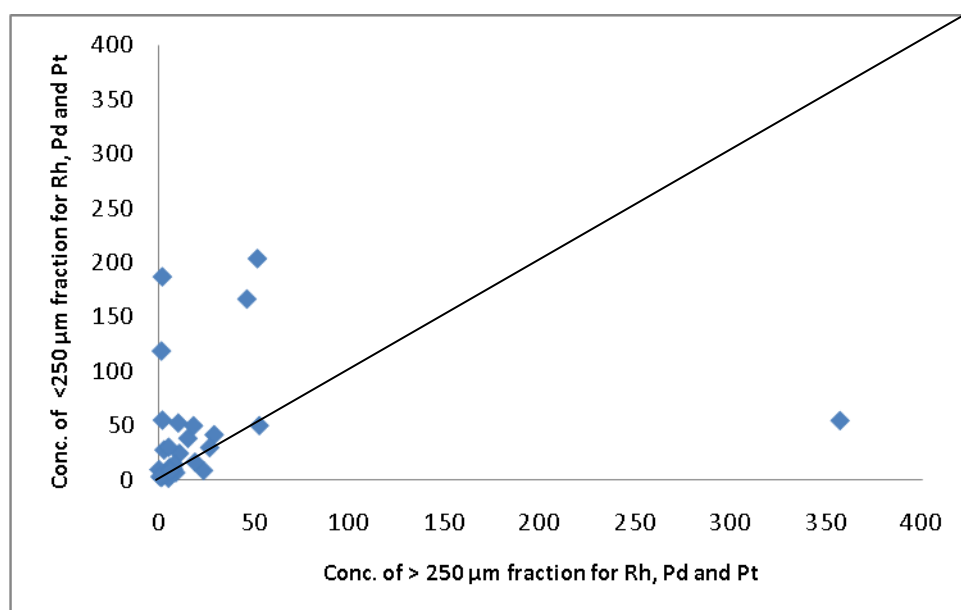


Figure 6.1: Comparison between the <250 and > the 250 μm size fraction for the PGEs

6.3.4 Grain-size partitioned PGE concentration and mass loading

Three road dust samples (8, 14 and 15) were separated into six grain size fractions. The variation in Pd, Pt and Rh concentrations across these particle size fractions is shown in Figure 6.3. A common assumption is that the <63 μm fraction is the most highly concentrated, as the typical relationship is an increase in element concentration with decreasing grain size (e.g.53, 54). This assertion reveals why most of the dominant fraction analysed for PGEs in soil by many researchers is the <63 μm size fraction

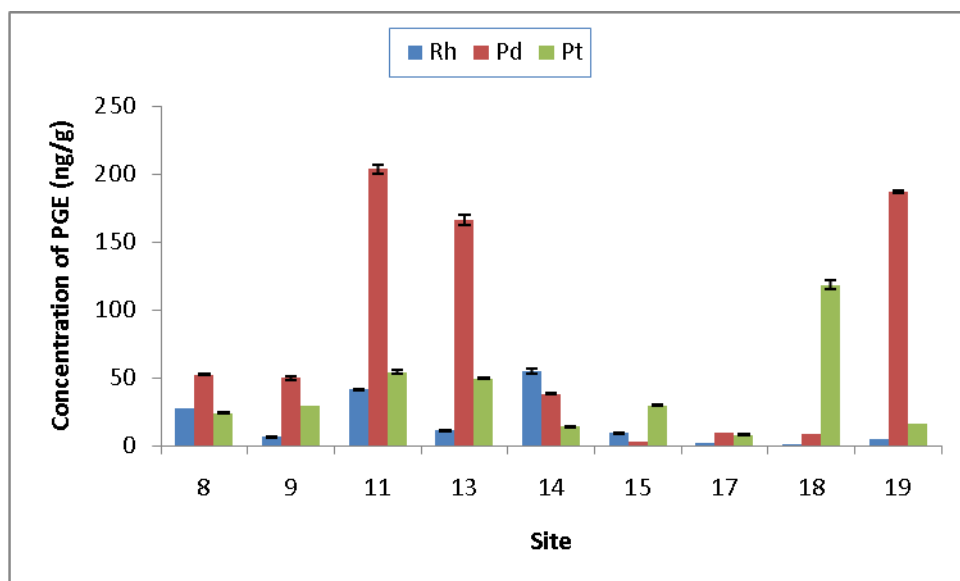


Figure 6.2: PGE concentrations in road dust

(e.g. 7, 9, 25, 42, 43, 49, 50, 55-59). However, this assumption is called into question in the present research as the result in Figure 6.3 show that a reasonable concentration of the PGEs can be obtained in other size fractions especially the 63 – 125 μm fractions.

Table 6.11: Global concentration of PGE in Road Dust (ng/g)

Location	^{105}Pd	^{195}Pt	^{103}Rh	Reference
San Diego (USA) 1985	38 – 280	100-680	-	51
Germany (1995)	1 – 146	-	-	52
Japan (1987)	297	-	-	60
Frankfurt (1995)	-	170	-	61
Richmond (UK)	-	0.42 – 29.8	-	23
Nottingham (UK) 1998	92.9	168.5	-	8
Birmingham (UK) 1997	-	6.48	-	8
London (UK)	-	73.7	-	62
Styria (Austria) 1994	4.0	55	10.3	63
Candid (DE) 1997	47.7	-	-	29
Dortmund	-	12	-	64
Graz Austria	-	14.5	-	51
Belgium	-	12.04	-	65
Rome (Italy)	102 – 504	14.4 – 62.2	1.9 – 11.1	49
Goteborg, Sweden	80	196	93	45
Madrid	-	317	74	7
Scotland	-	13 - 335	-	24
Bialystok, Poland	36.6	-	-	63
Bialystok, Poland	37.5	110.7	19.6	50
Perth (Austrelia)	58.1 – 440.4	53.8 – 419.4	8.8 – 91.4	21
Ioannina (NW Greece)	2.1 – 18.2	3.2 - 306	6.1 – 64.6	48

Similar work carried out by Sutherland et al. 2008 (66) observed that most of the concentration of PGEs are found in the coarser grain size fractions suggesting that analysis of only the < 63 µm fraction will underestimate the PGE concentration in the environmental sample.

Due to high concentration of the PGE found within specific grain size fractions and the differing contribution made by these fractions to the overall sediment mass, it was appropriate to calculate metal loadings (54). Platinum group elements loadings were calculated for physical grain size fractionated road dust samples. PGE loading values express pseudo-total grain specific PGE concentrations relative to the overall mass grain size percentage composition of individual road dust samples. The approach of Sutherland 2003b (59) was used in the computation of loading on the grain size fraction basis (GSF_{Load}).

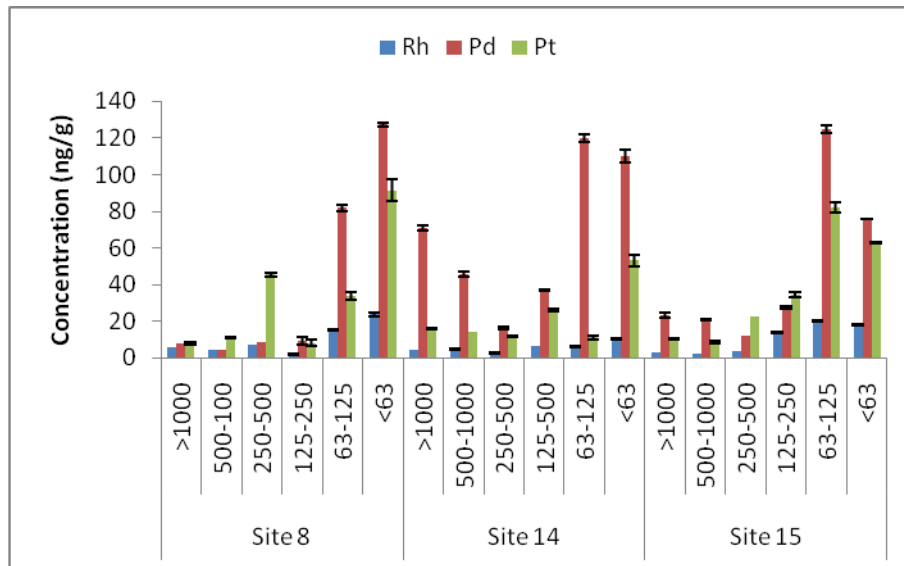


Figure 6.3: Grain-size (µm) partitioned PGEs concentration in three road dust sample (Site 8, 14 and 15) from Newcastle City Centre.

$$GSF_{Load} = \left[\frac{Rh_i \times GS_i}{\sum_{n=1}^6 Rh_i \times GS_i} \right] \times 100$$

Rh_i = Rhodium concentration in individual grain size eg < 63µm

GS_i = Mass percent of individual Rh_i = Rhodium fraction

$\sum_{n=1}^6 Rh_i$ = Summation of rhodium in the six size fractions.

Relative mass loading percentages per grain size fraction were determined for Pd, Pt and Rh for samples 8 14 and 15 as shown in Figure 6.4. For all the PGEs in the three sites, the

highest mass load was associated with the < 63 μm and the 63 - 125 μm . Maximum Pd loading were 53.3% in <63 μm , 30% in 63-125 μm and 43.9% in 63-125 μm in sites 8, 14 and 15 respectively. The maximum Pt mass loading were 50.7% in <63 μm , 40.2% in < 63 μm and 37.1% in 63-125 μm in sites 8, 14 and 15 respectively. Lesniewska et al. 2004 (50) observed that the highest concentration of platinum group element was in the <75 μm hence suggesting that analysis of <63 μm only can lead to underestimation of PGEs. Mass loadings for PGEs had been reported in some literatures. Sutherland and Wei & Morrison (66, 67), in their work on grain size partitioning observed that mass loading of PGEs in <63 μm has the lowest percentage compared to the other size fractions. This finding further reveals that analysis of only <63 μm will result in the underestimation of the PGEs in the environmental sample.

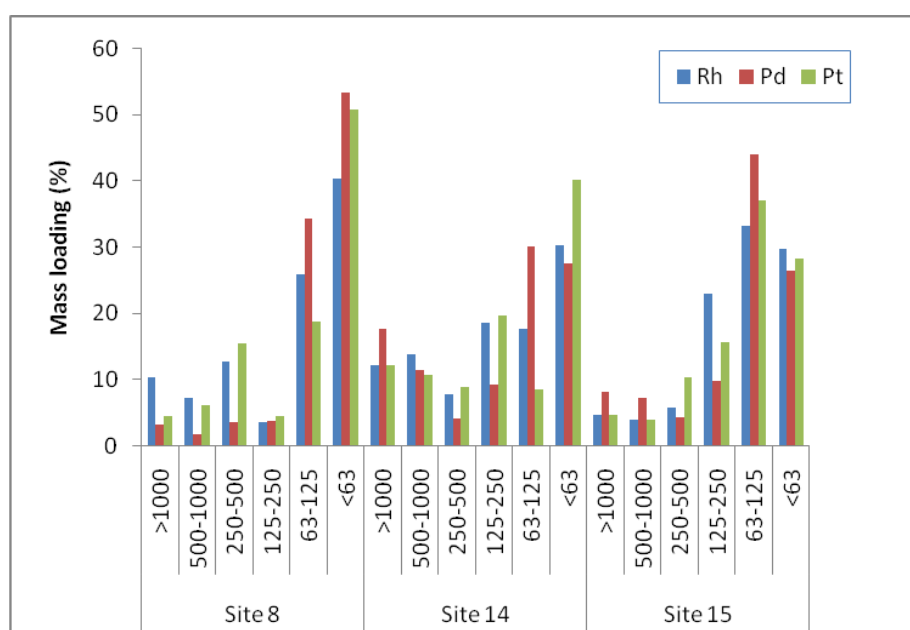


Figure 6.4: Relative PGE mass loading for sites 8, 14 and 15 across the 6 determined size fractions.

6.3.5 Correlation coefficient of PGE and PTEs concentration in road dust

To establish a relationship between platinum group elements (Rh, Pd and Pt) and PTEs, some sample points where both PTEs and PGE were measured (9, 11, 13, 17, 18 and 19) were chosen and correlation analysis carried out on them. The PTE concentrations for the selected

site are shown in Table 6.12 and the results of the correlation between the PTEs and PGEs shown in Table 6.13 in matrix form.

Lead and Cu are two of group of metals commonly associated with motor vehicle pollution

Table 6.12: PTE concentration road dust (mg/kg)

Site	As	Cd	Cu	Ni	Pb	Zn
9	4.4 ± 0.44	0.70 ± 0.22	140 ± 2.8	46.1 ± 3.4	409.0 ± 0.3	652 ± 4.1
11	6.2 ± 0.42	3.60 ± 0.08	217 ± 2	27.2 ± 2.5	2363.0 ± 0.4	543 ± 3.1
13	8.0 ± 0.40	1.01 ± 0.08	205 ± 2	22.0 ± 2.9	4261.0 ± 0.5	511 ± 3.4
17	7.0 ± 0.54	0.60 ± 0.14	192 ± 2	24.9 ± 3.2	1312.0 ± 0.4	635 ± 0.6
18	6.3 ± 0.52	1.60 ± 0.09	146 ± 2.6	22.8 ± 3.4	153.4 ± 0.4	469 ± 2.6
19	6.4 ± 0.62	0.90 ± 0.14	125 ± 2.8	28.8 ± 2.8	134.0 ± 0.3	351 ± 2.7

(32, 56, 68, 69), and both indicate a strong positive correlation in Table 6.14. Due to its use in fuel, Pb has historically been used as an indicator of traffic derived pollution.

Table 6.13: Relationship of PGEs with PTEs

	As	Cd	Cu	Ni	Pb	Zn	Rh	Pd	Pt
As	1.000								
Cd	-0.025 (0.963)	1.000							
Cu	0.538 (0.271)	0.508 (0.303)	1.000						
Ni	-0.890 (0.018)	-0.219 (0.677)	-0.449 (0.371)	1.000					
Pb	0.670 (0.145)	0.233 (0.656)	0.829 (0.041)	-0.416 (0.412)	1.000				
Zn	-0.316 (0.541)	-0.089 (0.867)	0.379 (0.459)	0.436 (0.387)	0.145 (0.784)	1.000			
Rh	-0.010 (0.985)	0.908 (0.012)	0.643 (0.168)	-0.052 (0.921)	0.447 (0.375)	0.068 (0.898)	1.000		
Pd	0.262 (0.616)	0.479 (0.336)	0.284 (0.586)	-0.142 (0.788)	0.472 (0.345)	-0.499 (0.313)	0.658 (0.156)	1.000	
Pt	0.030 (0.955)	0.391 (0.443)	-0.028 (0.958)	-0.343 (0.506)	-0.045 (0.933)	-0.226 (0.667)	0.050 (0.925)	-0.214 (0.684)	1.000

Pearson correlation with p-values in bracket

Whereas some studies have demonstrated strong positive correlation between the PGEs and Pb (32, 70), in this study Pb has no strong mathematical correlation with any of the PGEs. The lack of a strong correlation between PGE and Pb is not surprising as the introduction and growth of the use of catalytic converters in automobiles reduces drastically the emission of Pb from the automobile to the environment. Rhodium has a strong correlation with Cu and Cd (Table 6.13) as well as Pd. A common source is likely and possibly anthropogenic, e.g. automobiles.

6.3.6 PGE ratios for determining emission source

Platinum group element ratios are of great importance in determining automotive catalysts as emission sources (71). Commonly bivariate PGE ratios in a given sample media are compared to those associated with typical values in autocatalysts (66). Similarities between them have been used as evidence to infer anthropogenic contamination from catalytic converters (66). Three common ratio fields for three way catalytic converters (TWC) have been defined as follows:- Pt/Pd 1 – 2.5; Pt/Rh 5 – 16 and Pd/Rh 4 – 9 (70). The Pt/Pd, Pt/Rh and Pd/Rh observed in the present study are 0.56, 4.08 and 7.27 respectively. These values are obtained on n = 24 sample size. The Pt/Pd and Pt/Rh ratio in this study are not in agreement with the potential catalytic converter ratio defined by Ely et al., 2001 (70) and Whitney and Murray 2003 (21). This result appears to support the earlier assertion (section 6.1) of shift from Pt to Pd as component of TWC (6). The high Pd in our analysis results in the lower ratio of Pt/Pd, and the lower Pt results in the lower Pt/Rh ratio. The ratio of Pd/Rh is in agreement with that of Ely et al. 2001 (70). This suggests that the presence of Pd and Rh in the sampled points must have come from the automobile as a result of the deterioration of the TWC converter fitted at the exhaust of the motor vehicles.

6.4 Conclusion

From the present research, the following findings were made:-

1. Platinum group elements (Pd, Pt and Rh) for <250µm fraction of 9 urban street dust/sediment and 3 grain size fractionated samples from Newcastle city centre all indicate a strong anthropogenic signal.
2. The grain size analysis reveals that values of PGE are influenced by the size of the fraction analysed.

3. From grain size analysis, the highest concentration lies within the <63 and 63-125 μm size fraction. Therefore analysis of only the <63 μm will underestimate auto catalyst PGE.
4. There is a strong positive correlation between Pd and Rh and the Pd/Rh ratio (7.27) for Newcastle City Centre samples falls within the ratio field (4 – 9) defined by Ely et al. 2001 as indicative of TWC (70).
5. The low value of the Pt/Pd and the Pt/Rh ratio of the samples in comparison with other authors give an indication of a possible recent shift in the composition of the TWC converters from Pt towards Pd.

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Chapter Seven: Conclusion and future work

7.1 Conclusion

This research aimed to investigate the oral bioaccessibility of 7 PTEs (As, Cd, Cr, Cu, Ni, Pb and Zn) from former industrial site (St Anthony's lead works) now used for recreational activities. The pseudo total content, uptake by the foraged fruits and mobility of these PTEs by single extraction using EDTA and HOAc were examined. Furthermore, an investigation of the urban street dust from Newcastle city centre and its environs was performed to determine the elemental content, oral bioaccessibility and platinum group elements.

To achieve the research aims, the experiment were designed into sub-experiments. The first experiment was on the former industrial site and dealt with pseudo total PTE content and mobility of the PTEs using EDTA and HOAc. In addition, pH, organic matter contents, and CEC of the soil from the former site were measured. The mean pH, %LOI and CEC are 7.32, 11.47 and 28.61cmolc/kg respectively. The pseudo total PTE concentration varied from one sample point to the other across the site with Pb and Zn exhibiting the highest concentration in all the sampled points. The highest concentration of Pb, Zn and As from the sampled point is 33,306, 10,620 and 6,502 mg/kg respectively. Extractions of PTEs in the soils using chemical selective extractants (EDTA and HOAc) also varied across the sampled points but correlates positively with the pseudo total PTE concentration. The lowest percentage extraction was found in Cr (< 25%) and Ni (< 45%).

In the second experiment, foraged fruits obtained from the site for two seasons were analysed for pseudo total PTE content so as to assess the amount of PTEs taken up by the fruits. The PTEs availability for the foraged fruits was assessed by measuring the transfer factor (TF). It was found that the TF in all the sampled points (except Cd in SAL 1 in 2007) are significantly <1.00 in both seasons indicating that the majority of the element remained in the soil matrix. Therefore while the level of PTE in the soil is relatively high for some elements e.g. Pb, Zn and As, the suspected risk to human health based on soil-to-plant transfer ratio is negligible.

The possible implication to human health associated with accidental ingestion of the contaminated soil was assessed using the BARGE method in the third experiment. The results indicated that the bioaccessible fraction varied across the site and between the different PTEs but correlates positively with the pseudo total PTE content. All the PTEs measured have their

bioaccessibility more in the gastric + intestinal phase. Other types of measuring bioaccessibility used in this work such as single extraction and TDI/MDI relate differently to the BARGE experiment. Lead is the PTE of great concern in this site because the bioaccessible concentrations are higher than a typical soil intake required by a child to pose a risk. The work also shows that cautious estimates of bioaccessibility based on BARGE, have a role to play in the estimation of oral exposure during the development of site-specific assessment criteria. However, this use of conservatively estimated bioaccessibility should be justified on a site by site and substance by substance basis.

The fourth experiment was on the determination of pseudo total PTE content and their bioaccessibility through oral ingestion on road dust from the Newcastle city centre and its environs. The result obtained from the study indicates that the concentrations of the PTEs compared favourably with those of other cities in the world. The mean concentration decreases in the order: Pd (992 mg/kg) > Zn (421 mg/kg) > Cu (132 mg/kg) > Ni (26 mg/kg) > As (6.4 mg/kg) > Cd (1.0 mg/kg) with driving style (stop/start at intersections or traffic lights) having a more significant impact on the concentration than the volume of traffic. The bioaccessibility of road dust based on the worst case scenario indicates that Cd and Zn had the highest % bioaccessible fractions (> 45%) while As, Cu, Ni and Pb had lower % bioaccessible fractions (< 35%). None of the PTE measured was above the unintentional consumption of 0.1 g/day when compared with the TDI or MDI values hence are generally low to pose a risk.

The fifth experiment dealt on the evaluation of PGE and the effect of particle size on its distribution in urban road dust. The result obtained shows that the mean concentration decreases in the order: Pd (79.8 ng/g) > Pt (38.2 ng/g) > Rh (17.6 ng/g). Also the grain size analysis shows that most of the PGEs are found in the particle sizes 63-125 µm and < 63 µm therefore analyzing particle size of only 63 µm as practiced by most researchers will underestimate the PGE concentration in the environmental samples.

7.2 Future Work

The present work dealt on oral ingestion as the exposure pathway for assessing risk from metal contaminated site. However, development of tests to mimic the processes of other pathways such as inhalation leading to bioaccessibility via the lungs and dermal absorption leading to skin depot bioavailability need to be considered. Also bioaccessibility of other

contaminants such as organic substances and the platinum group elements need to be investigated in both sample matrices. Furthermore, a clear understanding of the interactions and mechanisms governing the contaminants dissolution from soil/dust in the human gastrointestinal tract also need to be investigated.

Appendix A

***In vitro* Extraction Test (BARGE METHOD): Application to soils from former St Anthony's Lead Works**

Arsenic (As)

Samples (SAL)	Pseudo-total (mg/kg)	Gastric (mg/kg)	Gastric + Intestinal (mg/kg)	% BAF
	Mean \pm SD (n = 3)	Mean \pm SD (n = 3)	Mean \pm SD (n = 3)	
1	19 \pm 1.7	5.0 \pm 1.4	9.9 \pm 1.6	52.1
2	59 \pm 1.4	14.4 \pm 1.1	25.7 \pm 2.1	43.6
3	905 \pm 3.6	226.4 \pm 4.8	375.9 \pm 3.0	41.5
4	140 \pm 0.8	48.7 \pm 3.4	79.1 \pm 4.6	56.5
5	140 \pm 0.6	41.3 \pm 3.8	73.9 \pm 4.2	52.9
6	1156 \pm 2.3	372.8 \pm 6.2	574.3 \pm 4.8	49.7
7	178 \pm 3.2	59.2 \pm 3.9	107 \pm 5.6	60.1
8	266 \pm 0.9	91.6 \pm 1.2	160.4 \pm 0.5	60.3
9	398 \pm 0.9	138.8 \pm 3.6	254.4 \pm 2.3	63.9
10	178 \pm 0.9	54.8 \pm 2.3	98.3 \pm 1.1	55.2
11	10 \pm 0.7	3.4 \pm 0.9	5.5 \pm 1.1	55.0
12	669 \pm 2.7	221 \pm 3.4	366 \pm 1.6	54.7
13	722 \pm 2.8	226 \pm 5.6	378 \pm 2.3	52.4
14	148 \pm 2.6	54.6 \pm 3.3	89.4 \pm 3.1	60.4
15	856 \pm 2.7	293 \pm 4.8	485 \pm 5.2	56.7
16	358 \pm 2.7	124 \pm 3.5	228 \pm 2.3	63.7
17	2816 \pm 4.6	996 \pm 21.6	1708 \pm 15.4	60.7
18	61 \pm 2.6	19 \pm 3.5	30 \pm 4.3	49.2
19	6502 \pm 2.9	2134 \pm 6.3	3366 \pm 3.4	51.8

Cadmium (Cd)

Samples (SAL)	Pseudo-total mg/kg	Gastric (mg/kg)	Gastric + Intestinal (mg/kg)	% BAF
	Mean \pm SD (n = 3)	Mean \pm SD (n = 3)	Mean \pm SD (n = 3)	
1	0.5 \pm 3.6	0.33 \pm 3.3	0.35 \pm 0.5	70.0
2	1.1 \pm 1.8	0.69 \pm 2.4	0.74 \pm 1.6	67.3
3	36.8 \pm 0.2	19.03 \pm 0.3	26.63 \pm 0.5	72.4
4	2.2 \pm 1.8	1.6 \pm 1.1	2.1 \pm 0.4	95.5
5	3.0 \pm 1.5	1.3 \pm 0.7	2.0 \pm 2.5	66.7
6	10.2 \pm 1.5	4.1 \pm 4.1	6.9 \pm 0.7	67.6
7	2.7 \pm 1.4	1.5 \pm 0.6	2.06 \pm 2.3	76.3
8	3.7 \pm 1.2	2.5 \pm 0.9	2.9 \pm 2.3	78.4
9	9.0 \pm 1.8	5.4 \pm 0.7	7.1 \pm 1.7	78.9
10	2.8 \pm 1.1	1.6 \pm 0.7	1.9 \pm 2.6	67.9
11	0.4 \pm 2.4	0.3 \pm 2.5	0.30 \pm 1.3	75.0
12	24.5 \pm 2.2	13.8 \pm 7.5	15.5 \pm 1.3	63.3
13	12.0 \pm 1.6	8.5 \pm 3.1	9.8 \pm 1.7	81.7
14	7.9 \pm 4.9	4.2 \pm 1.1	4.7 \pm 2.6	59.5
15	13.5 \pm 1.4	6.5 \pm 3.9	8.1 \pm 4.8	60.0
16	9.8 \pm 1.7	5.7 \pm 6.7	6.8 \pm 1.3	69.4
17	23.6 \pm 1.0	11.02 \pm 3.9	16.72 \pm 6.2	70.8
18	1.8 \pm 9.9	0.74 \pm 15.1	1.12 \pm 12.6	62.2
19	43.7 \pm 0.9	17.7 \pm 2.5	29.3 \pm 6.3	67.1

Chromium (Cr)

Samples (SAL)	Pseudo-total (mg/kg)	Gastric (mg/kg)	Gastric + Intestinal (mg/kg)	% BAF
	Mean \pm SD (n = 3)	Mean \pm SD (n = 3)	Mean \pm SD (n = 3)	
1	70 \pm 0.9	29 \pm 0.54	52.0 \pm 0.96	74.3
2	84 \pm 0.6	21.7 \pm 0.3	42.5 \pm 1.1	50.6
3	81 \pm 5.9	22.3 \pm 3.2	42.2 \pm 8.3	52.1
4	75 \pm 0.8	17.1 \pm 3.4	29.0 \pm 7.8	38.7
5	74 \pm 1.0	22.5 \pm 3.8	33.8 \pm 6.6	45.7
6	84 \pm 4.7	22.9 \pm 1.9	35.5 \pm 7.4	42.3
7	107 \pm 7.2	18.6 \pm 2.5	30.8 \pm 6.6	28.8
8	74 \pm 1.0	25.6 \pm 4.5	41.0 \pm 2.9	55.4
9	93 \pm 6.9	22.6 \pm 2.6	41.0 \pm 5.8	44.0
10	93 \pm 6.9	21.5 \pm 2.3	38.9 \pm 5.7	41.8
11	82 \pm 0.9	21.2 \pm 5.1	35.6 \pm 1.7	43.4
12	164 \pm 0.8	43 \pm 3.3	75.0 \pm 8.8	45.7
13	543 \pm 0.7	112 \pm 2.2	214.0 \pm 11.7	39.4
14	117 \pm 1.1	41.5 \pm 4.5	72.0 \pm 2.1	61.5
15	620 \pm 0.6	208 \pm 2.9	400.0 \pm 21	64.5
16	116 \pm 1.2	42 \pm 3.7	55 \pm 7	47.4
17	121 \pm 0.3	41.6 \pm 3.9	61.1 \pm 9.5	50.5
18	402 \pm 1.1	102 \pm 6.7	175 \pm 9.8	43.5
19	93 \pm 0.9	32 \pm 4.7	49 \pm 10.4	52.7

Copper (Cu)

Samples (SAL)	Pseudo-total (mg/kg)	Gastric (mg/kg)	Gastric + Intestinal (mg/kg)	% BAF
	Mean \pm SD (n = 3)	Mean \pm SD (n = 3)	Mean \pm SD (n = 3)	
1	46 \pm 3.7	14.6 \pm 6.0	33.5 \pm 3.5	72.8
2	70 \pm 2.1	20.0 \pm 1.3	43.4 \pm 5.0	62.0
3	501 \pm 0.4	131.4 \pm 2.0	330.3 \pm 1.9	65.9
4	61.8 \pm 1.9	16.3 \pm 1.9	42.6 \pm 3.7	68.9
5	99 \pm 1.1	26.5 \pm 0.8	62.1 \pm 2.9	62.7
6	598 \pm 2.9	129.6 \pm 2.7	391.5 \pm 4.2	65.5
7	214 \pm 4	15.5 \pm 5.8	157.5 \pm 1.07	73.6
8	147 \pm 1.3	26.7 \pm 0.6	103 \pm 2.4	70.1
9	238 \pm 4.7	27.5 \pm 1.4	151.5 \pm 1.7	63.7
10	127 \pm 1.7	21.9 \pm 0.7	85.6 \pm 2.5	67.4
11	22 \pm 1.5	6.2 \pm 3.2	15.9 \pm 4.1	72.3
12	320 \pm 1.7	109 \pm 1.1	248.0 \pm 1.8	77.5
13	465 \pm 1.74	123 \pm 3.8	299 \pm 4.4	64.3
14	181 \pm 1.1	25.1 \pm 1.3	126.1 \pm 2.8	69.7
15	682 \pm 1.5	156 \pm 1.3	472 \pm 1.9	69.2
16	171 \pm 1.7	18.6 \pm 4.1	109.4 \pm 6.5	64.0
17	404 \pm 1.3	77.9 \pm 5.3	248.9 \pm 5.3	61.6
18	102 \pm 1.4	23.3 \pm 3.8	67.8 \pm 4.7	66.4
19	104.7 \pm 0.7	25.4 \pm 4.4	68.6 \pm 9.6	65.5

Nickel (Ni)

Samples (SAL)	Pseudo-total (mg/kg)	Gastric (mg/kg)	Gastric + Intestinal (mg/kg)	% BAF
	Mean \pm SD (n = 3)	Mean \pm SD (n = 3)	Mean \pm SD (n = 3)	
1	30.7 \pm 4.5	4.1 \pm 1.1	7.3 \pm 2.7	23.7
2	42.6 \pm 2.3	15.7 \pm 1.9	30.1 \pm 6.8	70.7
3	94.6 \pm 0.4	17.6 \pm 2.2	34.4 \pm 2.9	36.4
4	30.5 \pm 1.9	4.7 \pm 1.5	9.0 \pm 3.7	29.5
5	32.6 \pm 0.7	6.3 \pm 9.7	10.6 \pm 5.6	32.5
6	156.8 \pm 0.8	41.6 \pm 3.1	75.1 \pm 7.8	47.9
7	52.5 \pm 5.1	13.4 \pm 5.4	24.4 \pm 2.6	46.5
8	39.8 \pm 1.2	7.0 \pm 2.0	13.5 \pm 3.7	33.9
9	38.2 \pm 2.9	9.2 \pm 4.9	16.9 \pm 3.2	44.2
10	31 \pm 4.5	6.4 \pm 1.7	11.2 \pm 3.9	36.2
11	22.2 \pm 1.8	5.4 \pm 3.1	7.5 \pm 8.3	33.8
12	142 \pm 1.8	44.9 \pm 1.4	69.2 \pm 1.8	48.7
13	135 \pm 0.5	32.2 \pm 1.3	54.5 \pm 2.5	40.4
14	73 \pm 0.5	28.9 \pm 1.5	37.3 \pm 3.6	51.1
15	100 \pm 1.2	33.7 \pm 3.3	56.5 \pm 6.5	56.5
16	59 \pm 2.7	7.4 \pm 8.6	12.6 \pm 10.6	21.4
17	96 \pm 1.3	32.5 \pm 4.4	48.6 \pm 7.9	50.6
18	55 \pm 1.6	15.6 \pm 5.6	28.3 \pm 11.8	51.5
19	56 \pm 1.3	16.2 \pm 1.3	26.7 \pm 1.3	47.7

Lead (Pb)

Samples (SAL)	Pseudo-total (mg/kg)	Gastric (mg/kg)	Gastric + Intestinal (mg/kg)	% BAF
	Mean \pm SD (n = 3)	Mean \pm SD (n = 3)	Mean \pm SD (n = 3)	
1	174 \pm 0.4	65.5 \pm 5.0	94.0 \pm 3.0	54.0
2	1381 \pm 1.5	445 \pm 4.0	683 \pm 2.1	49.5
3	29302 \pm 7.9	7110 \pm 7.1	11916 \pm 4.5	40.7
4	1048 \pm 2.5	177 \pm 8.5	262 \pm 2.4	25.0
5	2452 \pm 1.9	644 \pm 4.3	1121 \pm 1.7	45.7
6	29286 \pm 5.3	6007 \pm 28	10360 \pm 26	35.4
7	5071 \pm 1.9	1981 \pm 6.9	2959 \pm 5.2	58.4
8	4833 \pm 1.6	1811 \pm 4.4	2331 \pm 0.9	48.2
9	7214 \pm 1.8	2044 \pm 4.5	3115 \pm 1.1	43.2
10	2691 \pm 1.3	666 \pm 3.6	995 \pm 1.1	37.0
11	221 \pm 3.2	73 \pm 8.7	119 \pm 8.5	53.8
12	17443 \pm 6	5013 \pm 2.8	7020 \pm 8.3	40.2
13	15024 \pm 10	3445 \pm 1.6	4448 \pm 9.6	29.6
14	4266 \pm 12	1277 \pm 6.5	1695 \pm 9.2	39.7
15	28709 \pm 28	8363 \pm 63	686 \pm 58	31.5
16	4968 \pm 16	1417 \pm 8.3	2652 \pm 5.5	53.4
17	22822 \pm 18	7377 \pm 7.1	10962 \pm 37.4	48.0
18	1338 \pm 15	553 \pm 4.6	700 \pm 5.8	52.3
19	33306 \pm 11	13653 \pm 4.7	15374 \pm 4.9	46.2

Zinc (Zn)

Samples (SAL)	Pseudo-total (mg/kg)	Gastric (mg/kg)	Gastric + Intestinal (mg/kg)	% BAF
	Mean \pm SD (n = 3)	Mean \pm SD (n = 3)	Mean \pm SD (n = 3)	
1	169 \pm 0.6	40.1 \pm 10.0	62.2 \pm 9.6	36.8
2	332 \pm 1.0	106.7 \pm 1.6	142 \pm 0.6	42.8
3	10620 \pm 5.6	3806 \pm 6.2	6013 \pm 2.1	56.6
4	427 \pm 3.4	156.5 \pm 12.2	209.4 \pm 5.2	49.0
5	540 \pm 1.9	209.7 \pm 5.1	265.3 \pm 2.4	49.1
6	5464 \pm 2.5	1588 \pm 6.9	2826 \pm 2.5	51.7
7	959 \pm 4.1	348.4 \pm 4.2	522.6 \pm 5.4	54.5
8	1522 \pm 4.3	616 \pm 2.8	881 \pm 3.0	57.9
9	2172 \pm 3.9	823 \pm 4.7	1159 \pm 2.8	53.4
10	879 \pm 4.7	385 \pm 5.1	454.2 \pm 4.7	51.7
11	123 \pm 1.1	31.1 \pm 6.6	52.9 \pm 7.7	43.0
12	3233 \pm 0.7	1180 \pm 14.5	1713 \pm 22.8	52.9
13	4355 \pm 0.8	1217 \pm 24	1975 \pm 31	45.4
14	2189 \pm 2.3	820 \pm 1.1	1355 \pm 3.1	61.9
15	7092 \pm 2.0	1747 \pm 30	2812 \pm 28	39.7
16	1133 \pm 1.6	473 \pm 2.0	641 \pm 2.9	56.6
17	8488 \pm 4.2	2299 \pm 2.8	3664 \pm 1.9	43.2
18	537 \pm 2.5	175 \pm 2.2	281 \pm 3.9	52.3
19	3268 \pm 1.2	1160 \pm 2.0	2011 \pm 4.0	61.5

Appendix B

Arsenic, cadmium and chromium bioaccessibility and pseudo-total data for 19 sample points.

As			Cd		Cr	
Samples (SAL)	Pseudo-total (mg/kg)	Bioaccessibility (mg/kg)	Pseudo-total (mg/kg)	Bioaccessibility (mg/kg)	Pseudo-total (mg/kg)	Bioaccessibility (mg/kg)
	Mean \pm SD (n = 3)	Mean \pm SD (n = 3)	Mean \pm SD (n = 3)	Mean \pm SD (n = 3)	Mean \pm SD (n = 3)	Mean \pm SD (n = 3)
1	19 \pm 1.7	9.9 \pm 1.6	0.5 \pm 3.6	0.35 \pm 0.5	70 \pm 0.9	52.0 \pm 0.96
2	59 \pm 1.4	25.7 \pm 2.1	1.1 \pm 1.8	0.74 \pm 1.6	84 \pm 0.6	42.5 \pm 1.1
3	905 \pm 3.6	375.9 \pm 3.0	36.8 \pm 0.2	26.63 \pm 0.5	81 \pm 5.9	42.2 \pm 8.3
4	140 \pm 0.8	79.1 \pm 4.6	2.2 \pm 1.8	2.1 \pm 0.4	75 \pm 0.8	29.0 \pm 7.8
5	140 \pm 0.6	73.9 \pm 4.2	3.0 \pm 1.5	2.0 \pm 2.5	74 \pm 1.0	33.8 \pm 6.6
6	1156 \pm 2.3	574.3 \pm 4.8	10.2 \pm 1.5	6.9 \pm 0.7	84 \pm 4.7	35.5 \pm 7.4
7	178 \pm 3.2	107 \pm 5.6	2.7 \pm 1.4	2.06 \pm 2.3	107 \pm 7.2	30.8 \pm 6.6
8	266 \pm 0.9	160.4 \pm 0.5	3.7 \pm 1.2	2.9 \pm 2.3	74 \pm 1.0	41.0 \pm 2.9
9	398 \pm 0.9	254.4 \pm 2.3	9.0 \pm 1.8	7.1 \pm 1.7	93 \pm 6.9	41.0 \pm 5.8
10	178 \pm 0.9	98.3 \pm 1.1	2.8 \pm 1.1	1.9 \pm 2.6	93 \pm 6.9	38.9 \pm 5.7
11	10 \pm 0.7	5.5 \pm 1.1	0.4 \pm 2.4	0.30 \pm 1.3	82 \pm 0.9	35.6 \pm 1.7
12	669 \pm 2.7	366 \pm 1.6	24.5 \pm 2.2	15.5 \pm 1.3	164 \pm 0.8	75.0 \pm 8.8
13	722 \pm 2.8	378 \pm 2.3	12.0 \pm 1.6	9.8 \pm 1.7	543 \pm 0.7	214.0 \pm 11.7
14	148 \pm 2.6	89.4 \pm 3.1	7.9 \pm 4.9	4.7 \pm 2.6	117 \pm 1.1	72.0 \pm 2.1
15	856 \pm 2.7	485 \pm 5.2	13.5 \pm 1.4	8.1 \pm 4.8	620 \pm 0.6	400.0 \pm 21
16	358 \pm 2.7	228 \pm 2.3	9.8 \pm 1.7	6.8 \pm 1.3	116 \pm 1.2	55 \pm 7
17	2816 \pm 4.6	1708 \pm 15.4	23.6 \pm 1.0	16.72 \pm 6.2	121 \pm 0.3	61.1 \pm 9.5
18	61 \pm 2.6	30 \pm 4.3	1.8 \pm 9.9	1.12 \pm 12.6	402 \pm 1.1	175 \pm 9.8
19	6502 \pm 2.9	3366 \pm 3.4	43.7 \pm 0.9	29.3 \pm 6.3	93 \pm 0.9	49 \pm 10.4

Appendix B

Copper, nickel and lead bioaccessibility and pseudo-total data for 19 sample points.

Cu			Ni		Pb	
Samples (SAL)	Pseudo-total (mg/kg)	Bioaccessibility (mg/kg)	Pseudo-total (mg/kg)	Bioaccessibility (mg/kg)	Pseudo-total (mg/kg)	Bioaccessibility (mg/kg)
	Mean \pm SD (n = 3)	Mean \pm SD (n = 3)	Mean \pm SD (n = 3)	Mean \pm SD (n = 3)	Mean \pm SD (n = 3)	Mean \pm SD (n = 3)
1	46 \pm 3.7	33.5 \pm 3.5	30.7 \pm 4.5	7.3 \pm 2.7	174 \pm 0.4	94.0 \pm 3.0
2	70 \pm 2.1	43.4 \pm 5.0	42.6 \pm 2.3	30.1 \pm 6.8	1381 \pm 1.5	683 \pm 2.1
3	501 \pm 0.4	330.3 \pm 1.9	94.6 \pm 0.4	34.4 \pm 2.9	29302 \pm 7.9	11916 \pm 4.5
4	61.8 \pm 1.9	42.6 \pm 3.7	30.5 \pm 1.9	9.0 \pm 3.7	1048 \pm 2.5	262 \pm 2.4
5	99 \pm 1.1	62.1 \pm 2.9	32.6 \pm 0.7	10.6 \pm 5.6	2452 \pm 1.9	1121 \pm 1.7
6	598 \pm 2.9	391.5 \pm 4.2	156.8 \pm 0.8	75.1 \pm 7.8	29286 \pm 5.3	10360 \pm 26
7	214 \pm 4	157.5 \pm 1.07	52.5 \pm 5.1	24.4 \pm 2.6	5071 \pm 1.9	2959 \pm 5.2
8	147 \pm 1.3	103 \pm 2.4	39.8 \pm 1.2	13.5 \pm 3.7	4833 \pm 1.6	2331 \pm 0.9
9	238 \pm 4.7	151.5 \pm 1.7	38.2 \pm 2.9	16.9 \pm 3.2	7214 \pm 1.8	3115 \pm 1.1
10	127 \pm 1.7	85.6 \pm 2.5	31 \pm 4.5	11.2 \pm 3.9	2691 \pm 1.3	995 \pm 1.1
11	22 \pm 1.5	15.9 \pm 4.1	22.2 \pm 1.8	7.5 \pm 8.3	221 \pm 3.2	119 \pm 8.5
12	320 \pm 1.7	248.0 \pm 1.8	142 \pm 1.8	69.2 \pm 1.8	17443 \pm 6	7020 \pm 8.3
13	465 \pm 1.74	299 \pm 4.4	135 \pm 0.5	54.5 \pm 2.5	15024 \pm 10	4448 \pm 9.6
14	181 \pm 1.1	126.1 \pm 2.8	73 \pm 0.5	37.3 \pm 3.6	4266 \pm 12	1695 \pm 9.2
15	682 \pm 1.5	472 \pm 1.9	100 \pm 1.2	56.5 \pm 6.5	28709 \pm 28	686 \pm 58
16	171 \pm 1.7	109.4 \pm 6.5	59 \pm 2.7	12.6 \pm 10.6	4968 \pm 16	2652 \pm 5.5
17	404 \pm 1.3	248.9 \pm 5.3	96 \pm 1.3	48.6 \pm 7.9	22822 \pm 18	10962 \pm 37.4
18	102 \pm 1.4	67.8 \pm 4.7	55 \pm 1.6	28.3 \pm 11.8	1338 \pm 15	700 \pm 5.8
19	104.7 \pm 0.7	68.6 \pm 9.6	56 \pm 1.3	26.7 \pm 1.3	33306 \pm 11	15374 \pm 4.9

Appendix B

Zinc bioaccessibility and pseudo-total data for 19 sample points.

Samples (SAL)	Pseudo-total (mg/kg)	Bioaccessibility (mg/kg)
	Mean \pm SD (n = 3)	Mean \pm SD (n = 3)
1	169 \pm 0.6	62.2 \pm 9.6
2	332 \pm 1.0	142 \pm 0.6
3	10620 \pm 5.6	6013 \pm 2.1
4	427 \pm 3.4	209.4 \pm 5.2
5	540 \pm 1.9	265.3 \pm 2.4
6	5464 \pm 2.5	2826 \pm 2.5
7	959 \pm 4.1	522.6 \pm 5.4
8	1522 \pm 4.3	881 \pm 3.0
9	2172 \pm 3.9	1159 \pm 2.8
10	879 \pm 4.7	454.2 \pm 4.7
11	123 \pm 1.1	52.9 \pm 7.7
12	3233 \pm 0.7	1713 \pm 22.8
13	4355 \pm 0.8	1975 \pm 31
14	2189 \pm 2.3	1355 \pm 3.1
15	7092 \pm 2.0	2812 \pm 28
16	1133 \pm 1.6	641 \pm 2.9
17	8488 \pm 4.2	3664 \pm 1.9
18	537 \pm 2.5	281 \pm 3.9
19	3268 \pm 1.2	2011 \pm 4.0

Appendix C

In vitro extraction test (BARGE METHOD): Application to Road dust from Newcastle City centre Newcastle upon Tyne NE England.

Arsenic (As)

Samples (Site)	Total (Microwave) (mg/kg)	Gastric (mg/kg)	Gastric + Intestinal (mg/kg)	% BAF
	Mean \pm SD (n = 3)	Mean \pm SD (n = 3)	Mean \pm SD (n = 3)	
1	8.6 \pm 4.6	1.6 \pm 6.6	3.1 \pm 8.7	36.1
2	4.4 \pm 5.3	0.6 \pm 7.0	1.0 \pm 14	22.7
3	4.4 \pm 4.4	0.7 \pm 9.6	1.2 \pm 10.6	27.3
4	6.2 \pm 4.2	1.2 \pm 2.5	1.9 \pm 4.9	30.6
5	8.0 \pm 4.0	1.5 \pm 6.3	2.9 \pm 5.5	36.3
6	6.0 \pm 4.5	0.6 \pm 11.1	1.1 \pm 17.7	18.3
7	7.0 \pm 5.4	0.9 \pm 9.4	1.7 \pm 14.4	24.3
8	6.3 \pm 5.2	0.7 \pm 13	1.3 \pm 15.5	20.6
9	6.4 \pm 6.2	0.9 \pm 6.3	2.7 \pm 12.2	42.2

Cadmium (Cd)

Samples (Site)	Total (Microwave) (mg/kg)	Gastric (mg/kg)	Gastric + Intestinal (mg/kg)	% BAF
	Mean \pm SD (n = 3)	Mean \pm SD (n = 3)	Mean \pm SD (n = 3)	
1	0.3 \pm 6.6	0.1 \pm 9.5	0.17 \pm 3.0	56.7
2	0.13 \pm 1.2	0.07 \pm 8.2	0.07 \pm 5.2	53.8
3	0.7 \pm 2.2	0.4 \pm 2.1	0.55 \pm 12.7	78.16
4	3.6 \pm 0.8	1.5 \pm 1.1	1.9 \pm 2.0	52.8
5	1.01 \pm 0.8	0.2 \pm 1.1	0.3 \pm 4.6	29.7
6	0.23 \pm 4.7	0.03 \pm 4.1	0.03 \pm 3.2	13.0
7	0.60 \pm 1.4	0.2 \pm 2.9	0.3 \pm 2.9	50.0
8	1.6 \pm 0.9	0.4 \pm 3.5	0.4 \pm 3.2	25.0
9	0.9 \pm 3.4	0.23 \pm 3.4	0.32 \pm 8.2	35.6

Copper (Cu)

Samples (Site)	Total (Microwave) (mg/kg)	Gastric (mg/kg)	Gastric + Intestinal (mg/kg)	% BAF
	Mean \pm SD (n = 3)	Mean \pm SD (n = 3)	Mean \pm SD (n = 3)	
1	67.2 \pm 2.6	9.5 \pm 3.1	23.3 \pm 3.5	34.7
2	25.3 \pm 3.7	Nil	6.1 \pm 5.1	24.1
3	140 \pm 2.8	7.5 \pm 3.8	42.3 \pm 4.1	30.2
4	217 \pm 2.0	65.6 \pm 1.6	74.1 \pm 3.4	64.0
5	205 \pm 2.0	30.7 \pm 1.6	66.6 \pm 3.5	32.5
6	59.8 \pm 2.4	Nil	1.6 \pm 8.0	2.7
7	192 \pm 2.0	35.8 \pm 2.2	55.3 \pm 5.1	28.8
8	146 \pm 2.6	5.0 \pm 6.0	7.6 \pm 8.9	5.2
9	125 \pm 2.8	3.1 \pm 1.7	12.0 \pm 1.9	9.6

Nickel (Ni)

Samples (Site)	Total (Microwave) (mg/kg)	Gastric (mg/kg)	Gastric + Intestinal (mg/kg)	% BAF
	Mean \pm SD (n = 3)	Mean \pm SD (n = 3)	Mean \pm SD (n = 3)	
1	19.1 \pm 2.5	2.9 \pm 5.4	5.3 \pm 6.1	27.7
2	13.7 \pm 3.5	3.5 \pm 6.4	6.0 \pm 7.3	43.8
3	46.1 \pm 3.4	2.7 \pm 2.3	6.7 \pm 2.5	14.5
4	27.2 \pm 2.5	4.4 \pm 1.2	8.8 \pm 1.1	32.4
5	22.0 \pm 2.9	5.9 \pm 0.8	8.4 \pm 3.6	38.2
6	25.0 \pm 2.7	1.3 \pm 2.5	2.1 \pm 5.2	8.4
7	24.9 \pm 3.2	3.2 \pm 1.3	6.9 \pm 1.7	27.7
8	22.8 \pm 3.4	0.7 \pm 5.3	2.2 \pm 3.4	9.6
9	28.8 \pm 2.8	0.7 \pm 22.7	2.3 \pm 13.1	8.0

Lead (Pb)

Samples (Site)	Total (Microwave) (mg/kg)	Gastric (mg/kg)	Gastric + Intestinal (mg/kg)	% BAF
	Mean \pm SD (n = 3)	Mean \pm SD (n = 3)	Mean \pm SD (n = 3)	
1	101 \pm 0.4	32.6 \pm 1.3	32.6 \pm 1.21	32.3
2	70.2 \pm 0.3	12.5 \pm 0.8	22.1 \pm 0.3	31.5
3	409 \pm 0.3	8.3 \pm 0.6	13.8 \pm 1.4	3.4
4	2363 \pm 0.4	850 \pm 0.4	1349 \pm 0.8	57.1
5	4261 \pm 0.5	1405 \pm 0.4	1586 \pm 0.7	37.2
6	127 \pm 0.3	35.6 \pm 3.0	47.5 \pm 0.9	37.4
7	1312 \pm 0.4	483 \pm 7.0	501 \pm 4.0	38.2
8	153.4 \pm 0.4	18.3 \pm 2.0	29.2 \pm 0.1	19.1
9	134 \pm 0.3	0.04 \pm 0.16	0.04 \pm 0.11	0.02

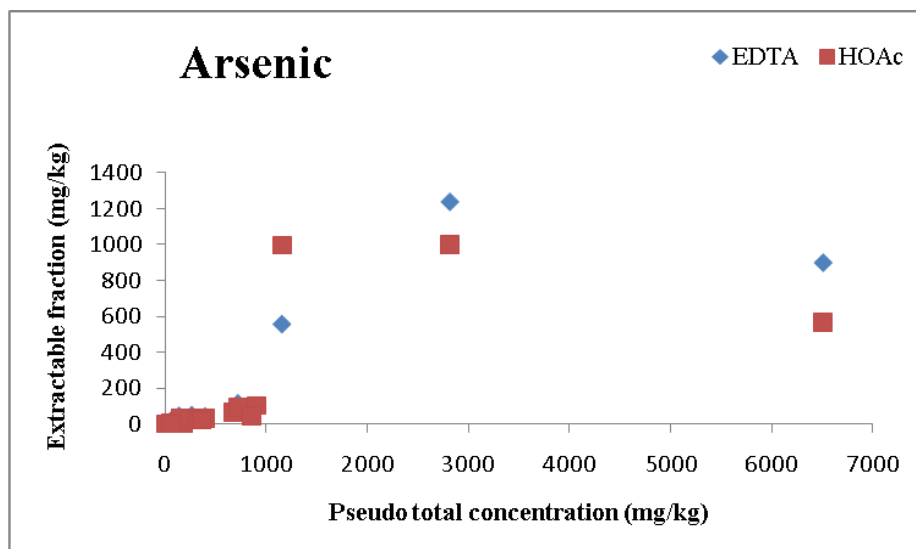
Zinc (Zn)

Samples (Site)	Total (Microwave) (mg/kg)	Gastric (mg/kg)	Gastric + Intestinal (mg/kg)	% BAF
	Mean \pm SD (n = 3)	Mean \pm SD (n = 3)	Mean \pm SD (n = 3)	
1	328 \pm 3.8	101 \pm 3.5	182.5 \pm 5.0	55.6
2	111 \pm 4.1	49.2 \pm 4.3	63.6 \pm 5.2	57.3
3	652 \pm 4.1	231.8 \pm 3.9	347 \pm 4.9	53.2
4	543 \pm 3.1	160 \pm 2.5	217 \pm 4.2	40.0
5	511 \pm 3.4	168 \pm 2.4	328 \pm 4.8	64.2
6	189 \pm 2.6	59.8 \pm 4.6	98.7 \pm 5.0	52.2
7	635 \pm 0.6	239 \pm 3.0	323.6 \pm 5.3	51.0
8	469 \pm 2.6	160 \pm 5.4	214.3 \pm 5.0	45.7
9	351 \pm 2.7	96.9 \pm 2.4	139.2 \pm 3.8	39.7

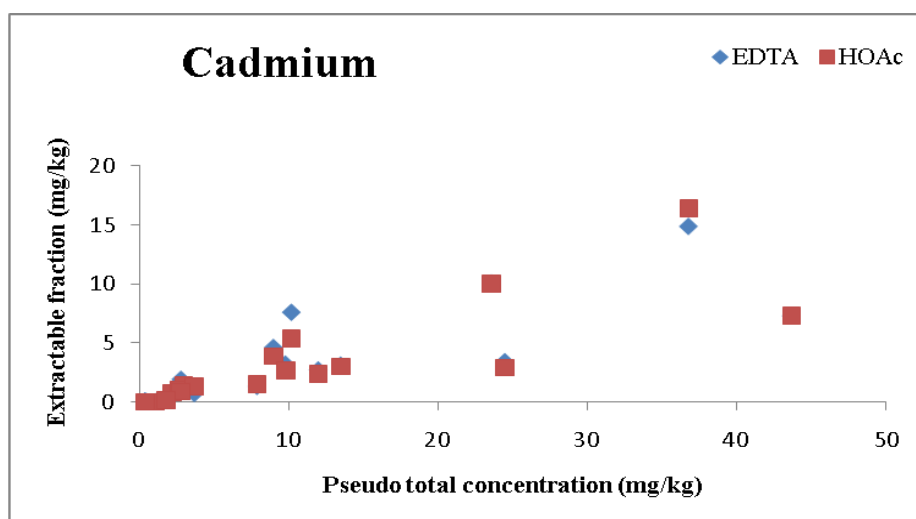
Appendix D

Correlation graph between the pseudo total concentration and the single extractions

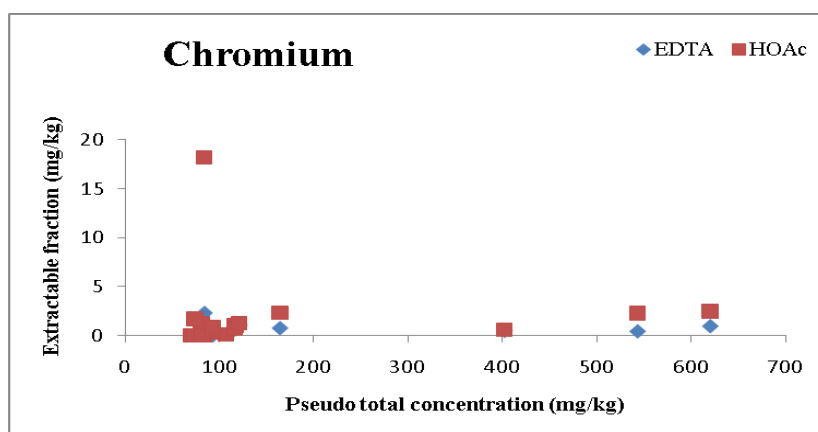
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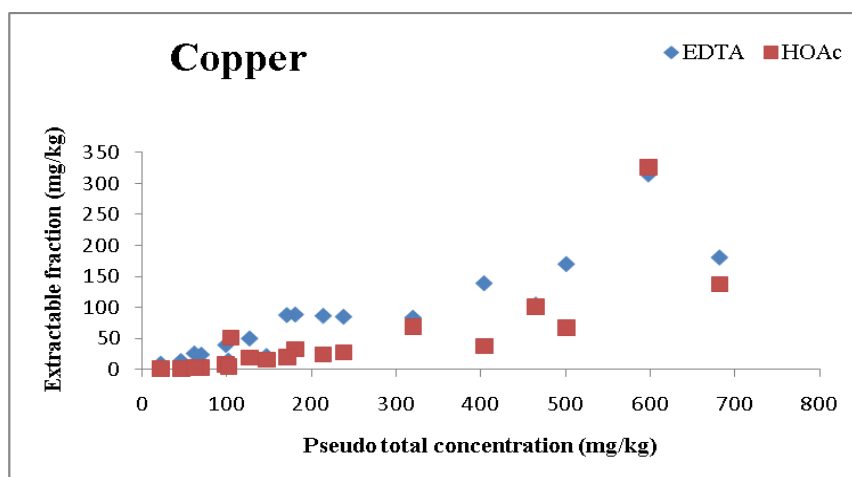
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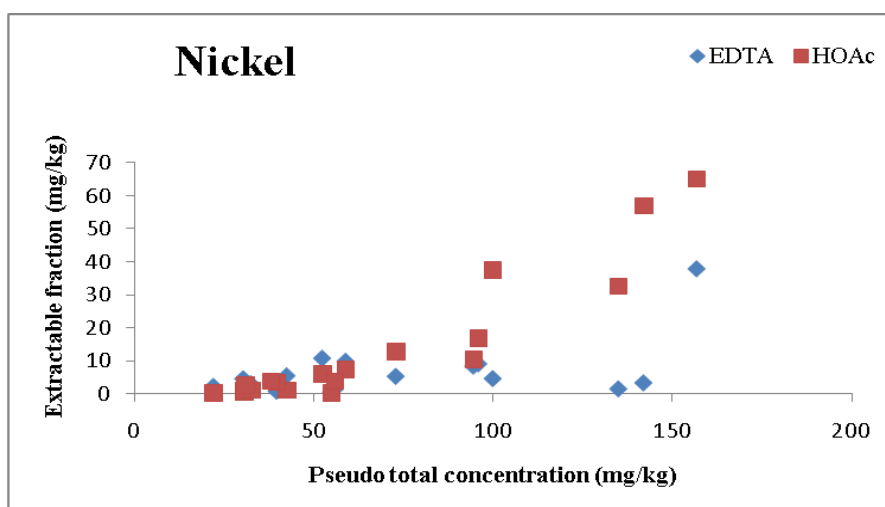
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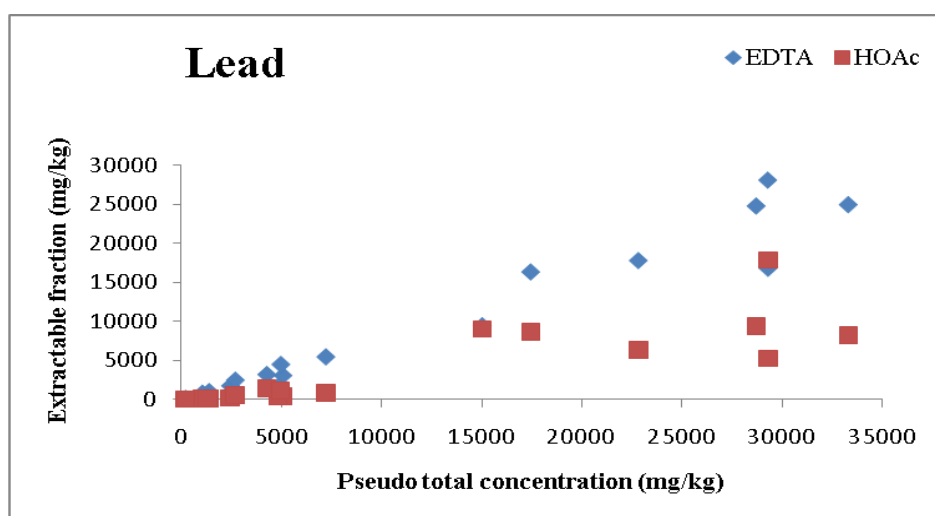
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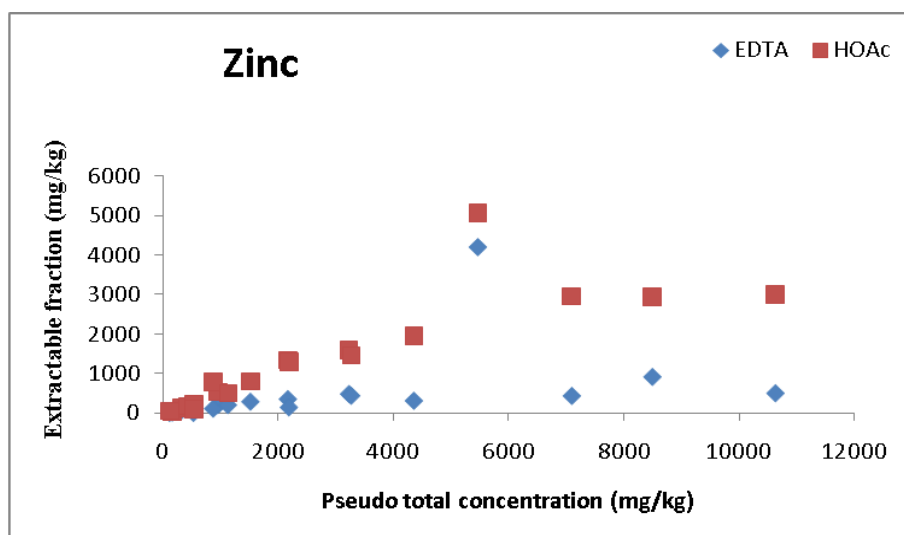
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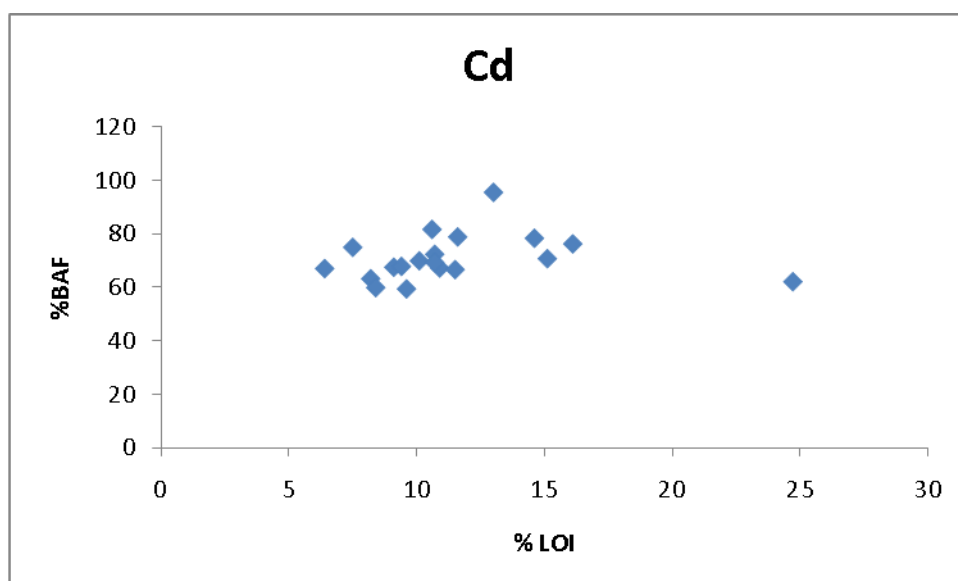
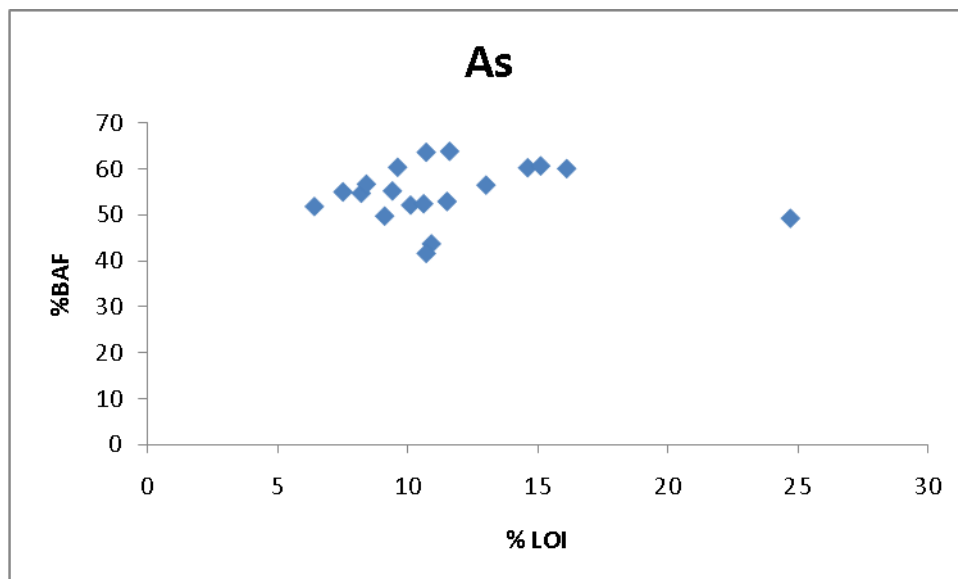


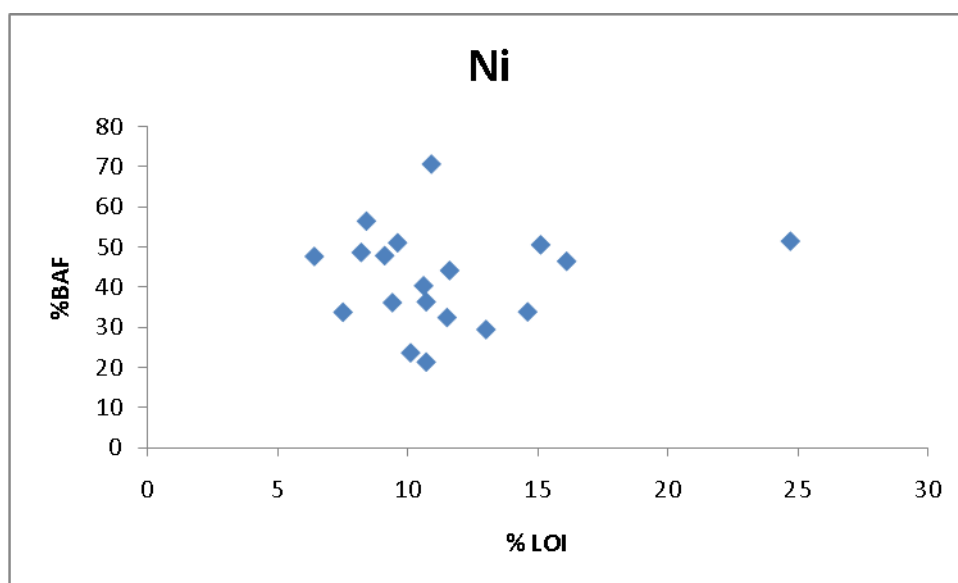
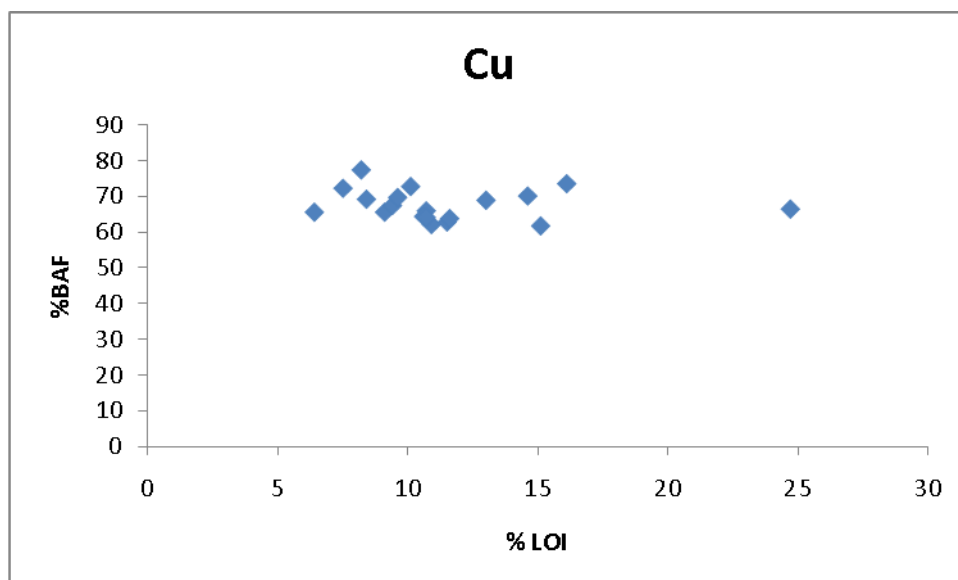
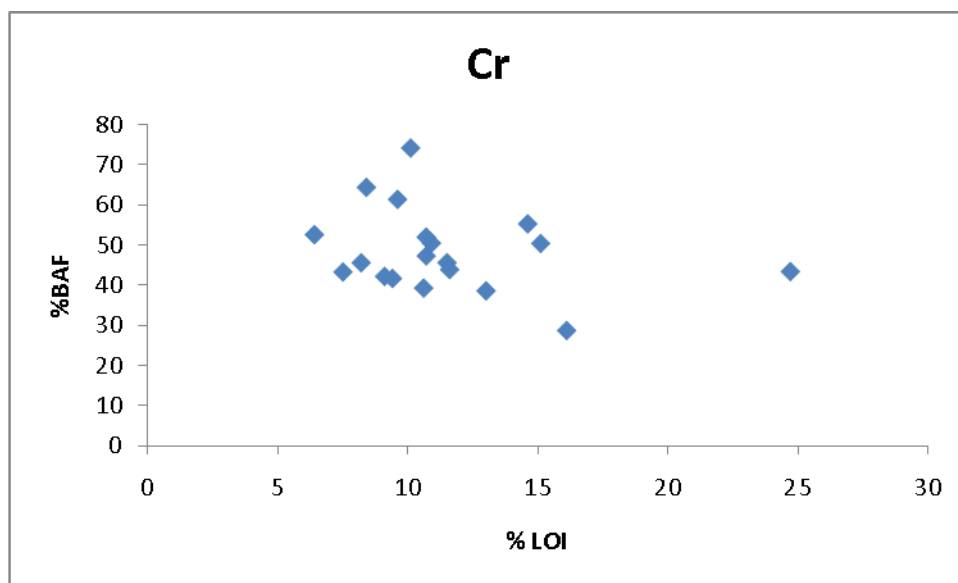
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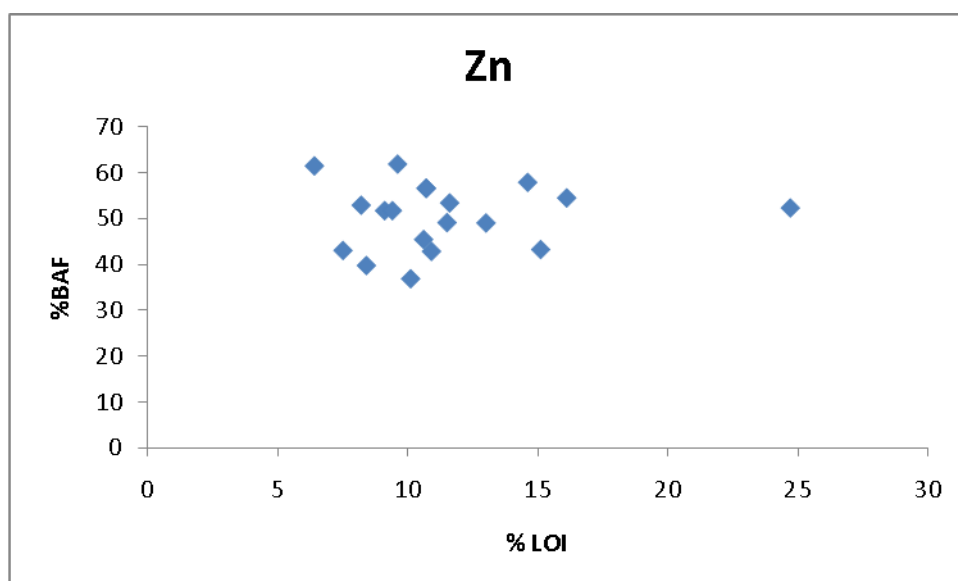
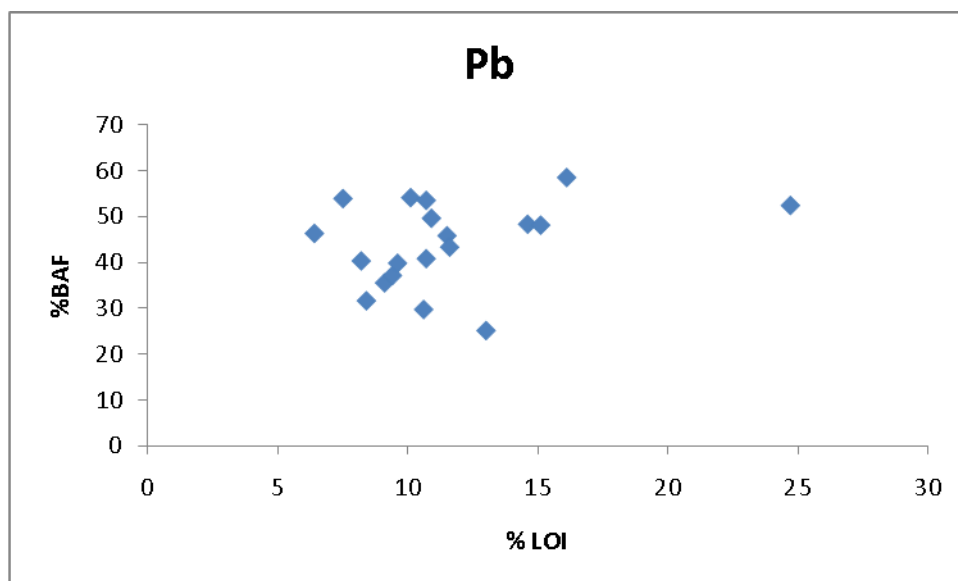


Appendix E

Plot of % BAF against % LOI for each of the PTE studied at St Anthony's lead works







Appendix F

Graphical relationship between traffic volume and pseudo total concentration of individual PTE in urban road dust of Newcastle upon Tyne

